

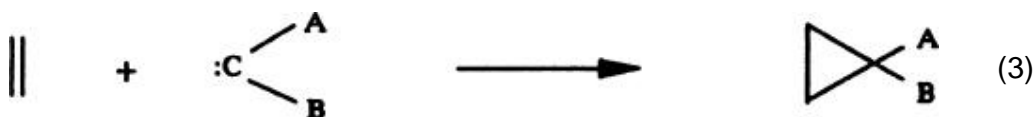
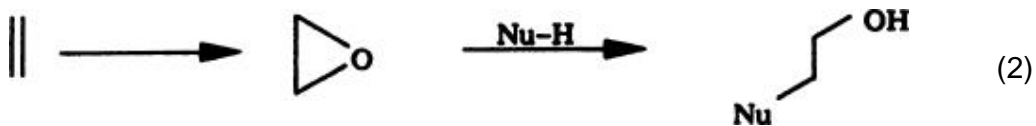
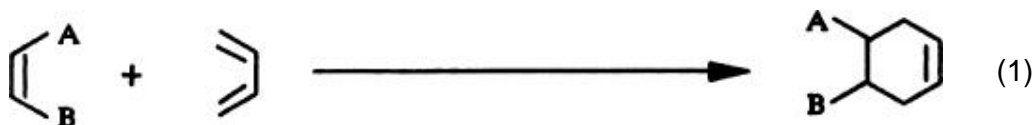
Tandem Vicinal Difunctionalization: β -Addition to α, β -Unsaturated Carbonyl Substrates Followed by α -Functionalization

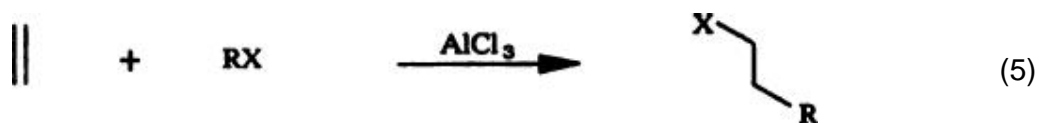
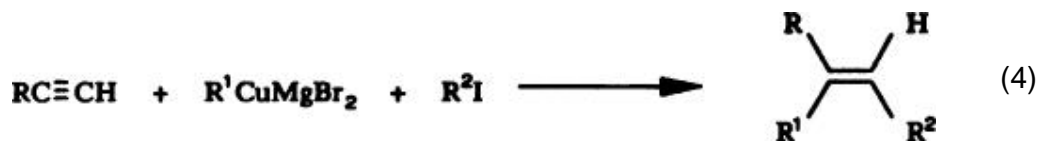
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1. Introduction

Vicinal difunctionalization reactions play an important role in modern synthetic organic chemistry. They provide access to complex structures in a stereocontrolled fashion and act as powerful, attractive, convergent elements in synthetic strategy. Consequently, examples of these reactions are numerous. (1) Among them may be cited the Diels–Alder reaction (Eq. 1), (2, 3) which results in vicinal dialkylation of a dienophile; epoxidation–functionalization of alkenes which results in 2-substituted alkanols (Eq. 2); (4) carbenoid additions to alkenes (Eq. 3) resulting in cyclopropanes; (5) organometalation–functionalization of alkynes (Eq. 4) (6) giving vicinally disubstituted alkenes, and the additions of alkyl halides (7) and acyl halides (8) to alkenes using Friedel–Crafts catalysts (Eq. 5). [2 + 2] Photocycloadditions (9, 10) and 1,3-dipolar cycloadditions (11) are but two of many more examples. New reactions are introduced regularly, such as radical cyclization–trapping, which recently has been applied to a synthesis of prostaglandin $F_{2\alpha}$. (12)

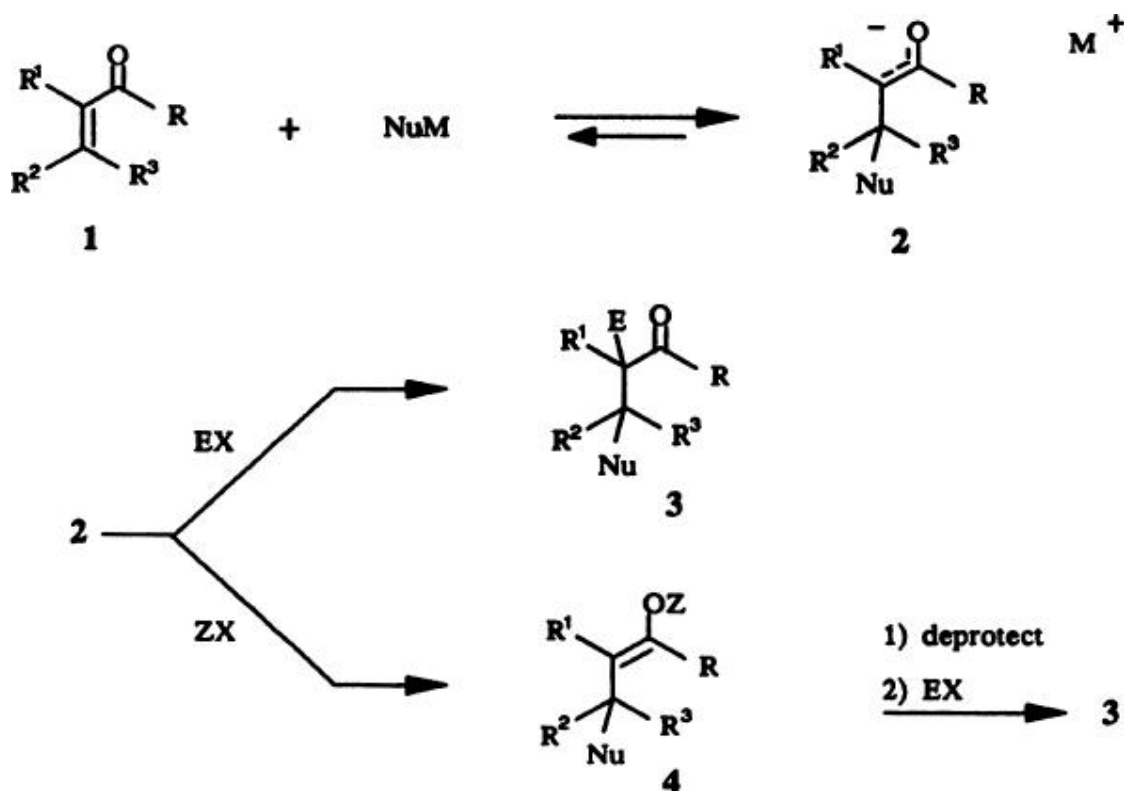




1.1. Definition of Tandem Vicinal Difunctionalization

Over the past 20 years, the process of tandem vicinal difunctionalization of α , β -unsaturated carbonyl substrates has been fully developed and extensively exploited. The tandem vicinal difunctionalization consists of two reactions, one enabling the other. An initial Michael (conjugate or 1,4) addition of a nucleophile, NuM, to the substrate **1** (the “Michael acceptor”) under aprotic conditions transforms both the α and β carbons. The β carbon is further substituted and the α carbon takes on nucleophilicity as an enolate ion **2** (the “conjugate enolate,” [Scheme 1](#)). The conjugate enolate ion subsequently may be trapped in situ using an appropriate electrophile, EX, thus derivatizing the α carbon. Conceptually, this can be envisaged as a vinylogous reaction. Through a “third-party” two-carbon extension, nucleophile and electrophile have reacted.

Scheme 1.



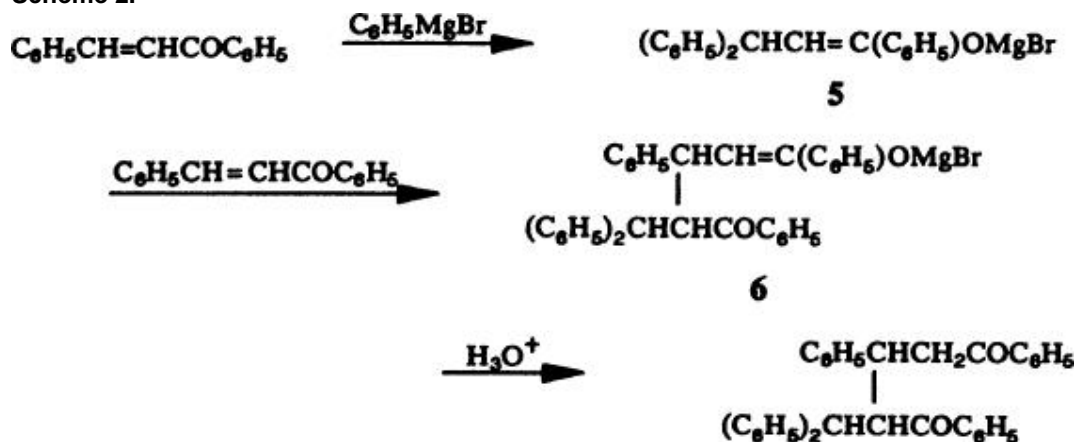
The enolate ion generated by the conjugate addition process, however, need not be α -functionalized in situ. As an ambident anion, it also may be isolated as a neutral species (4, an “enolate equivalent”) by O-functionalization using an appropriate protecting agent, ZX, or by proton quenching. After isolation of this enolate equivalent 4, the enolate may be regenerated by some means and then functionalized at the α carbon to give the vicinally disubstituted product 3. Inasmuch as extensive chemistry can be performed on species of structure 4 before final α -functionalization, the scope of tandem vicinal difunctionalizations of α , β -unsaturated carbonyl compounds for this review includes only (a) conjugate additions to the substrate followed by α -carbon functionalization in situ, (b) generation of a neutral species via conjugate addition, then regeneration of the conjugate enolate followed by α -carbon functionalization, and (c) generation of a neutral species via conjugate addition, followed by a single chemical modification before regeneration of the conjugate enolate and subsequent α -carbon functionalization.

Often, the general reaction sequence may be named more specifically as a tandem vicinal dialkylation or dicarbacondensation, (13, 14) referring to the fact that many of the reactions that have been performed create two new vicinal carbon–carbon bonds. Noncarbon nucleophiles and electrophiles also have become popular, resulting in vicinal carbon–heteroatom bonds in the products of the reaction sequence; for this reason the broader appellation, tandem vicinal difunctionalization, is at times more appropriate.

1.2. History

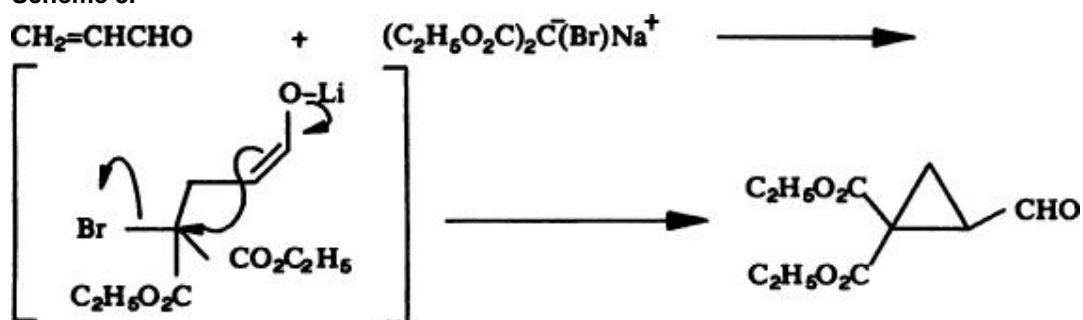
Early investigations of the reaction between α , β -unsaturated ketones and Grignard reagents showed that a large excess of the Grignard reagent was necessary to prevent the formation of undesired, "secondary" products. The nature of such products was unclear. (15) Gradual recognition that the conjugate addition process led to an adduct enolate (e.g., 5), (16) which itself was capable of competing with the Grignard reagent for the α , β -unsaturated ketone substrate (6), allowed the conclusion that the secondary products were dimers (Scheme 2). (17) These products subsequently were identified by unambiguous synthesis.

Scheme 2.



Realization of the potential synthetic utility (18, 19) of such observations and development of tandem vicinal difunctionalization as a general synthetic technique apparently was an equally slow process. In 1948, Warner (20) allowed acrolein to react with ethyl bromomalonate, presumably to obtain 4,4-diethoxycarbonyl-3-butenal via a 1,4 addition followed by dehydrohalogenation. Reexamination of the principal product clearly indicated that net cyclopropanation had occurred instead. By means of an $\text{S}_{\text{N}}1$ reaction, the newly appended bromomalonate moiety had C-alkylated the conjugate enolate (Scheme 3).

Scheme 3.

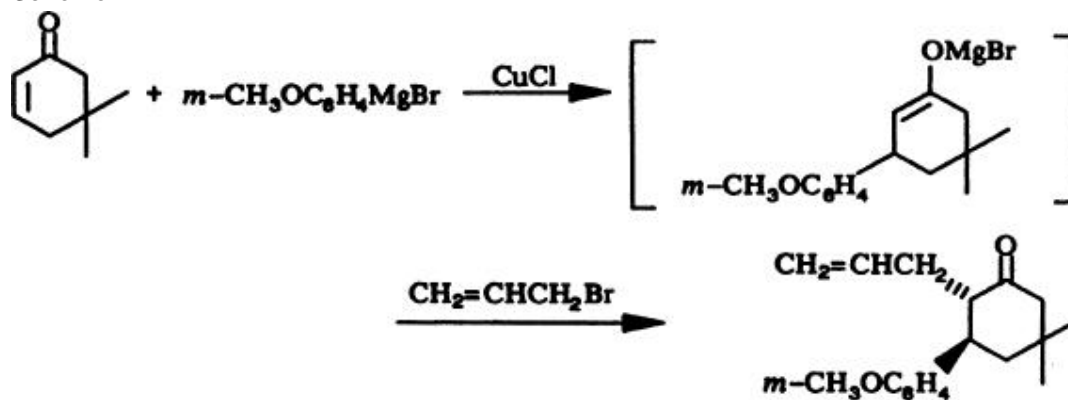


Similarly, base-initiated dimerizations of 2-cyclohexenones, known to give crystalline solids, (21, 22) remained mechanistically puzzling for some time before sequential Michael addition was suggested to account for some of the possible products. (23) It was not until 1969 that dimerization of 4,4-dimethyl-2-cyclopentenone under basic conditions was reported and the product unambiguously identified. (24)

Stork, (25) while investigating new methods for the regiospecific generation of enolates,

reported that the dissolving metal conjugate reduction of α , β -unsaturated ketones produced enolates, which could be C-alkylated under suitable conditions. Soon the concept was extended to include the conjugate additions of nucleophiles, resulting in the first one-pot, 3-component tandem vicinal difunctionalization reaction, which was used as a key step in the total synthesis of lycopodine (Scheme 4). (26)

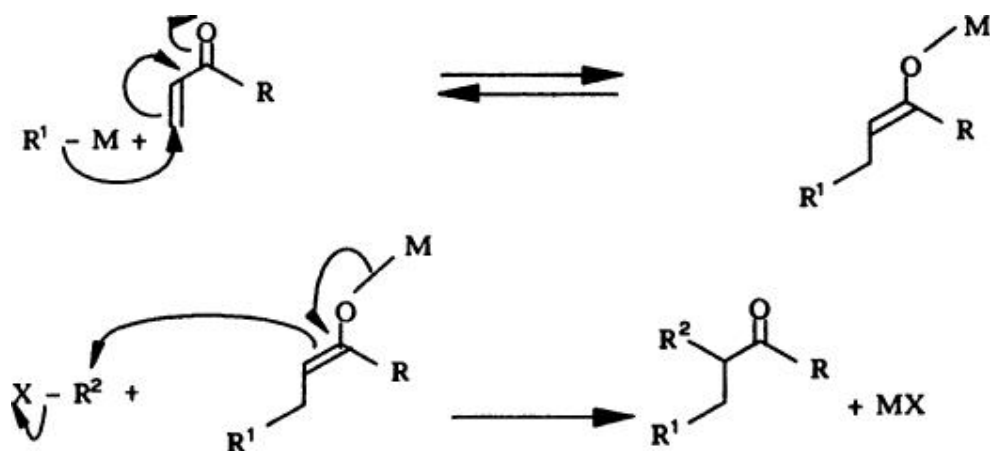
Scheme 4.



2. Mechanism

The overall reaction links two distinct bond-forming steps, both of which are well studied as to mechanism: a first step consisting of organometallic 1,4 addition to an α, β -unsaturated carbonyl substrate and a second step wherein the conjugate enolate is C-functionalized. It can be sketched along the lines of the process depicted in [Scheme 5](#). Conceptually appealing and perhaps operationally adequate to predict product distributions from tandem vicinal difunctionalization reactions, this model belies the complexity of the steps of which it is composed.

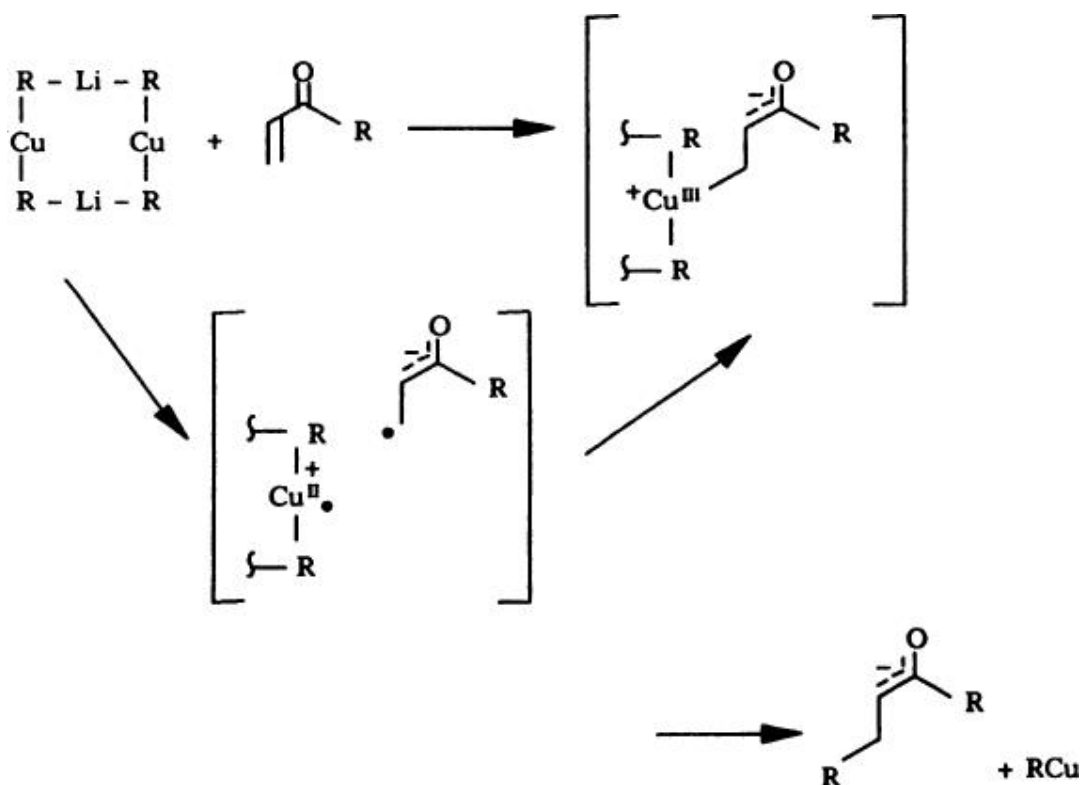
Scheme 5.



2.1. Step One— β -Addition to α, β -Unsaturated Carbonyl Substrates

The precise mechanism of the conjugate addition reaction has been debated for some time, ([27-32](#)) and undoubtedly varies according to the nature of the attacking nucleophile. ([33, 34](#)) In the case of the most common organocopper nucleophiles, a detailed mechanism remains to be determined, ([35-39](#)) but there is general agreement on its fundamental aspects: ([40](#)) oxidative *trans* addition of a d^{10} cuprate to the substrate producing a transient copper(III) (d^8) intermediate followed by reductive *cis* elimination generating the new chemical bond at the β carbon of the substrate and a conjugate enolate and copper(I) species ([Scheme 6](#)). Whether bond-forming occurs via direct nucleophilic oxidative addition, ([41, 42](#)) indirect single electron transfer–caged radical pair collapse, ([43-48](#)) or is preceded by copper(I)– π -bond coordination ([49-53](#)) continues to be investigated.

Scheme 6.

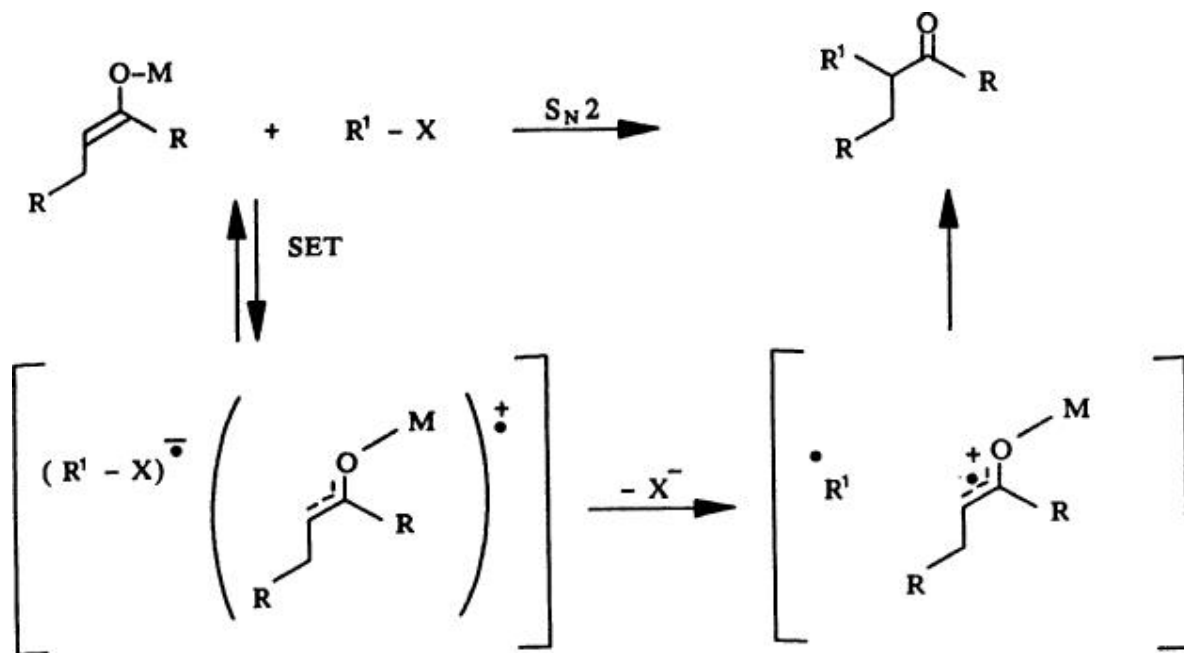


Mechanistic details of conjugate additions to α, β -unsaturated carbonyl substrates using less common, non-copper(II)-containing nucleophiles are not well determined. (54-56) Conjugate additions of Grignard reagents, for instance, appear to proceed by means of a single electron transfer mechanism; Michael additions of enolate anions may proceed by either single electron transfer or via an S_N2' -type process (*vide infra*).

2.2. Step Two—C-Functionalization of Enolates

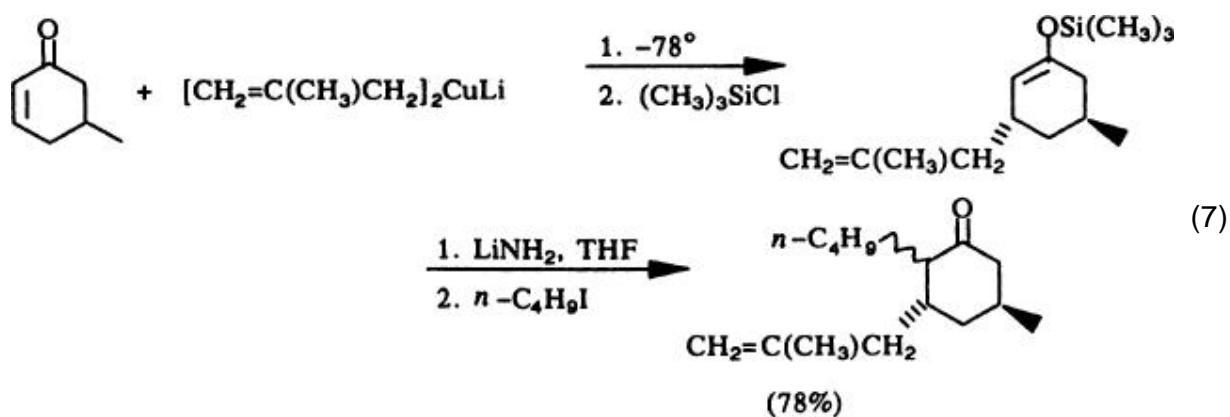
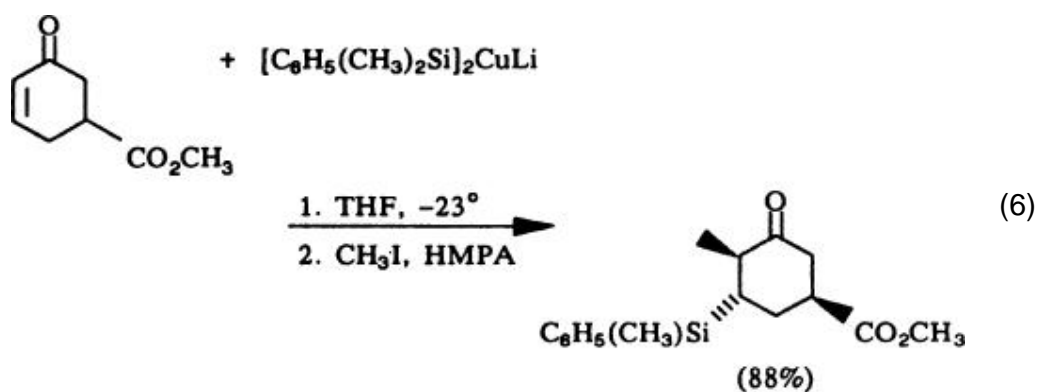
The counterion of the enolate is predetermined (57) by the first step of the tandem vicinal difunctionalization and can profoundly influence the reactivity and ambident nature of the enolate, (58) but otherwise the second step of the reaction is well described as a substitution reaction of an enolate with an electrophile. It is mechanistically identical to the C-alkylation of regioselectively generated enolates. (59) Recent research indicates that such additions may very well proceed by means of a single electron transfer mechanism, especially for electrophiles of lower reduction potentials (e.g., alkyl iodides); (60) electrophiles with higher reduction potentials (e.g., alkyl bromides) undergo bond formation based on the S_N2 process (Scheme 7). (61, 62)

Scheme 7.

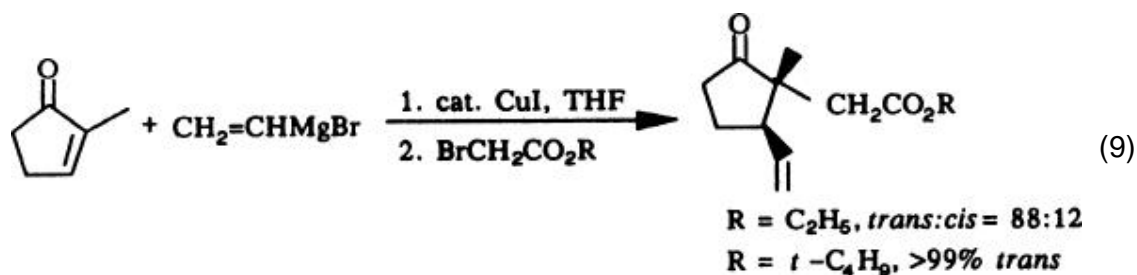
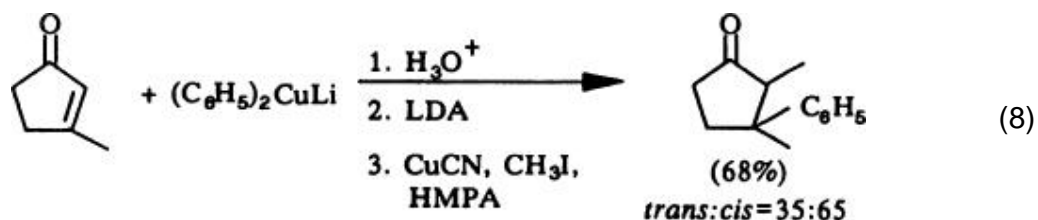


3. Stereochemistry

The conjugate addition reaction is unusually sensitive to the steric environment of the Michael acceptor. The bond-forming process at the β carbon of the substrate, therefore, adheres rather rigidly to steric approach control factors in determining the relative stereochemistry of the newly formed bond in the conjugate enolate. Thus, the 5-methoxycarbonyl group of 5-methoxycarbonyl-2-cyclohexenone directs axial attack of a silylcopper(I) reagent so that the 3,5-*trans*-disubstituted adduct is produced (Eq. 6; hexamethylphosphorictriamide, HMPA). (63) The effect of smaller directing groups is essentially the same (Eq. 7). (64) Comparison of these two examples, however, indicates that subsequent α -functionalization may not proceed with a similar degree of stereoselectivity. The thermodynamically more stable *trans* products usually predominate, as would be predicted by both steric approach and product development control arguments. (65, 66) A complex combination of factors, including the nature of the conjugate enolate, the enolate counterion, the reaction conditions, and the nature of the electrophile, can make predictions



somewhat unreliable. For example, when 3-methyl-2-cyclopentenone is reacted with diphenylcopperlithium and the conjugate enolate methylated (Eq. 8; lithium diisopropylamide, LDA), the *cis* and not the *trans* product predominates, a consequence of lithium–arene π –coordination. (67) The sterically remote alkoxy moiety of α -bromoacetates influences the stereochemical product distributions of the difunctionalization reaction of 2-methyl-2-cyclopentenone (Eq. 9). (68) It is worthwhile to bear in mind that if the product of the overall reaction possesses a tertiary α -carbon, equilibration can occur; this



process may or may not proceed at a rate sufficiently high to obscure the original stereochemical outcome of the initial α -functionalization of the conjugate enolate.

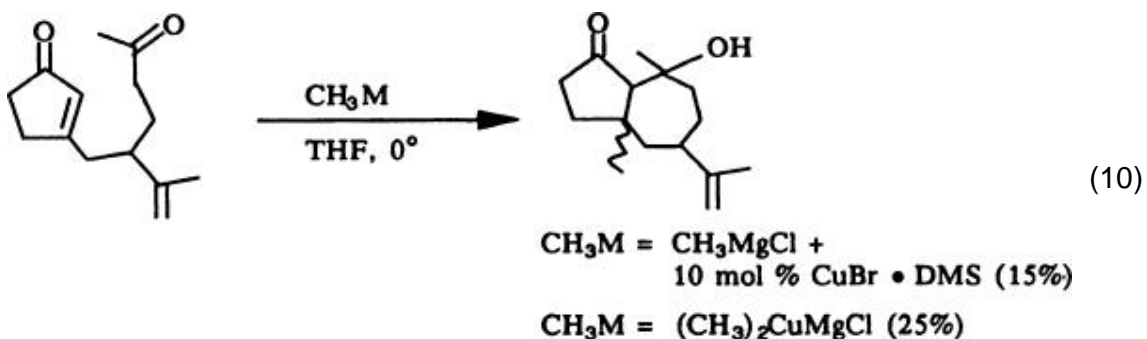
4. Scope and Limitations

4.1. Organocopper Reagents for β -Addition Followed by α -Functionalization

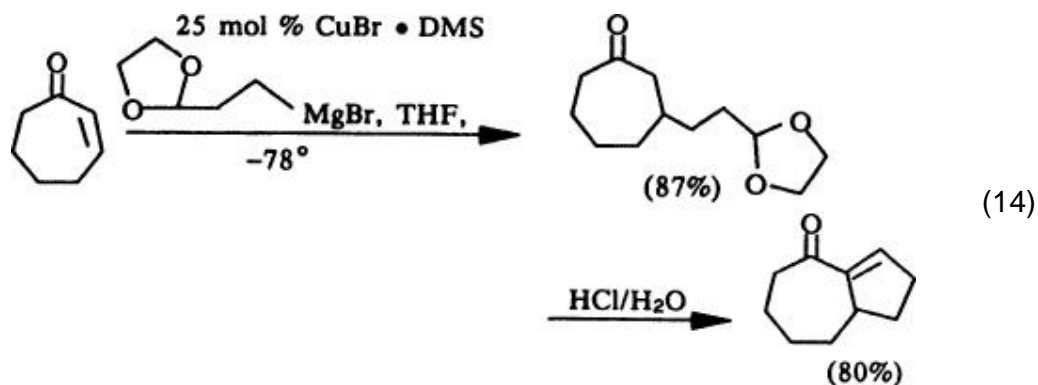
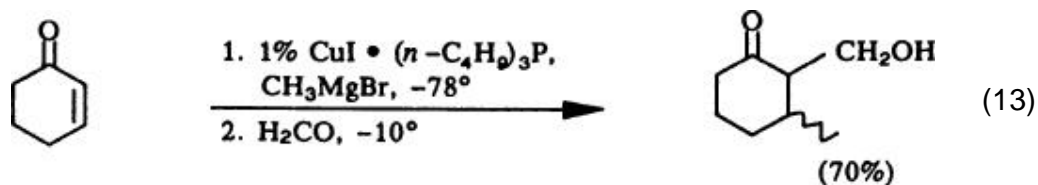
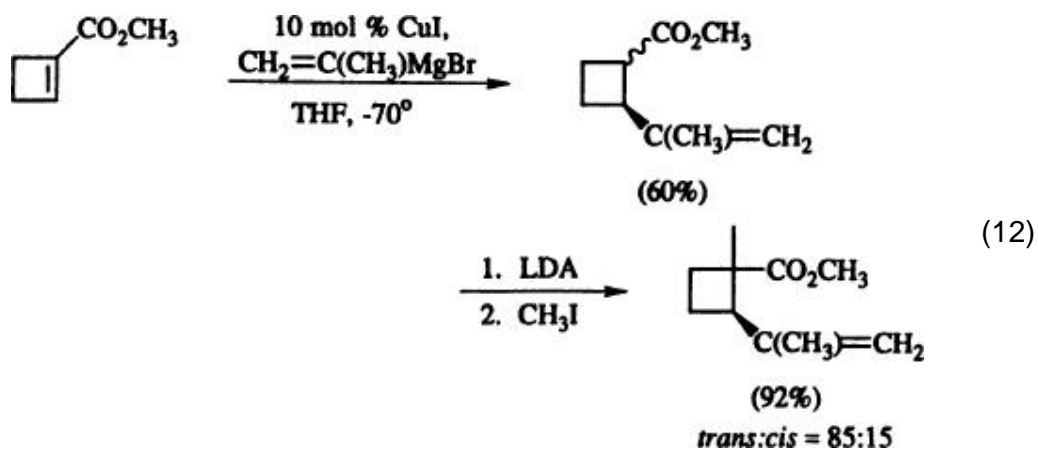
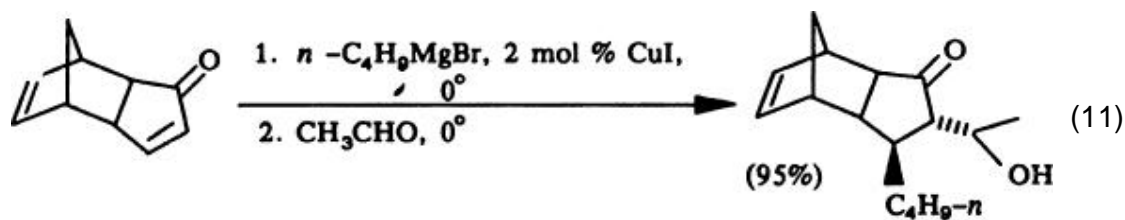
Nucleophilic organometallic 1,4 additions to α , β -unsaturated aldehydes, ketones, and esters have been and continue to be dominated by organocopper (Gilman) reagents, (69-71) largely because of the regioselectivity of these reagents for 1,4 versus 1,2 addition.

4.1.1.1. Catalytic Organocopper Reagents

Although the first example of a three-component tandem vicinal difunctionalization reaction was catalytic in organocopper [copper(I) chloride-catalyzed 1,4 addition of a Grignard reagent to 5,5-dimethyl-2-cyclohexenone (26)], these protocols (72) are not used widely when compared to stoichiometric organocopper reagents. The improvement in yield of the 1,4 adduct that is observed when stoichiometric organocopper reagents are utilized (e.g., Eq. 10; dimethyl sulfide, DMS) (73) most likely accounts for



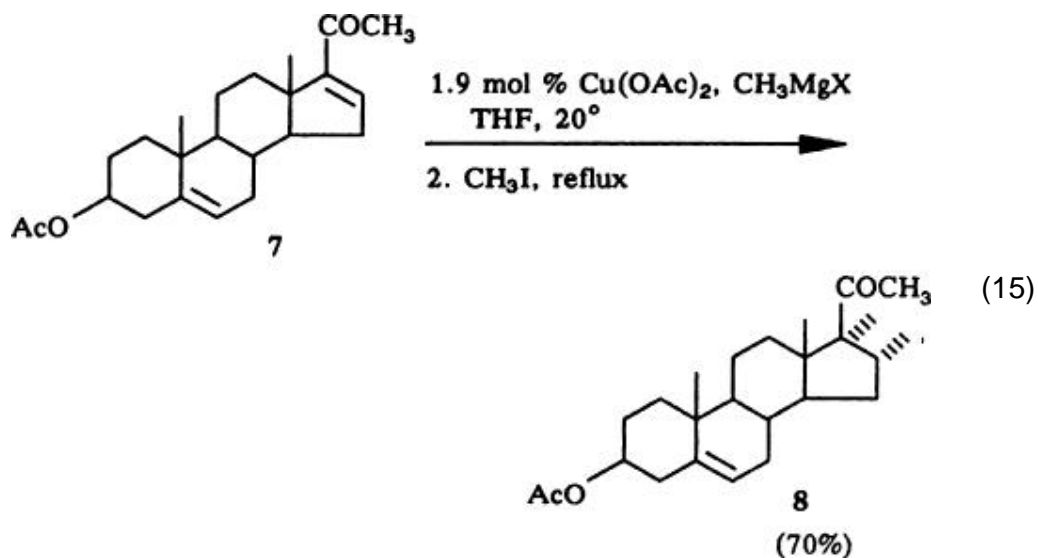
the preference. Nonetheless, conjugate additions catalyzed by copper(I) reagents can be highly successful. Typically, the organometallic reagent employed as the nucleophile is a Grignard reagent; the copper(I) halides, usually copper(I) iodide, copper(I) bromide, or their dimethyl sulfide or trialkylphosphine complexes, are present in amounts ranging from 2 to 10 mole percent (Eqs. 11 (74) and 12 (75)). Successful tandem vicinal dialkylations employing 1 mole percent of tris(tri-*n*-butylphosphino)copper(I) iodide have been reported (Eq. 13), (76) as have those using 25–30 mole percent of copper(I) bromide dimethyl sulfide complex as catalyst (Eq. 14). (77)



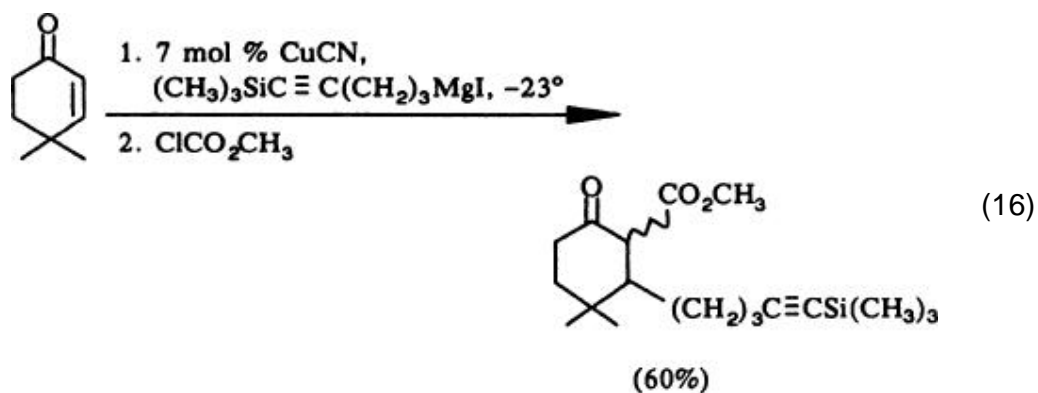
Explicit mention of the use of copper(II) catalysts is made rarely; conjugate addition of a methylmagnesium halide to steroid **7**, catalyzed by copper(II) acetate followed by α -methylation, gives steroid **8** in good yield (Eq. 15). (78)

The specific identity of the catalytically active organocopper species generated in situ during the reaction can have a critical effect on its outcome. Copper(I) halides complexed with solubilizing ligands are preferred because of added stability and ease of purification. Grignard reagents appear to perform more efficiently in copper(I)-catalyzed 1,4 additions than the analogous alkyllithium reagents.

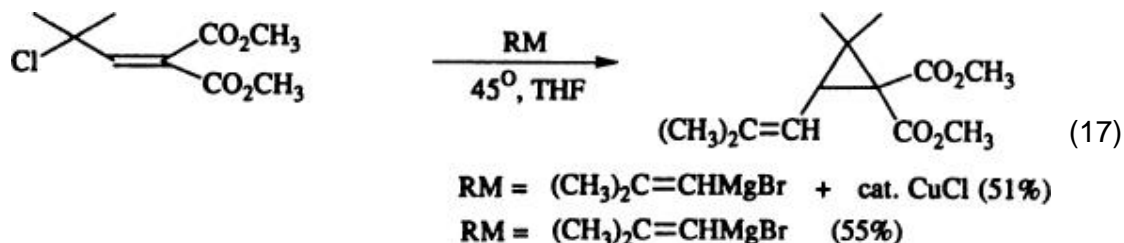
The ability to α -functionalize the conjugate enolate of copper(I) cyanide-catalyzed 1,4 addition to 4,4-dimethyl-2-cyclohexenone is determined by a combination of solvent (diethyl ether) and organomagnesium nucleophile (an alkylmagnesium iodide) (Eq. 16). (79) Use of tetrahydrofuran as solvent or an alkylmagnesium chloride instead of the analogous iodide leads exclusively to O-alkylation of the conjugate enolate. Copper(I) catalysis is imperative in



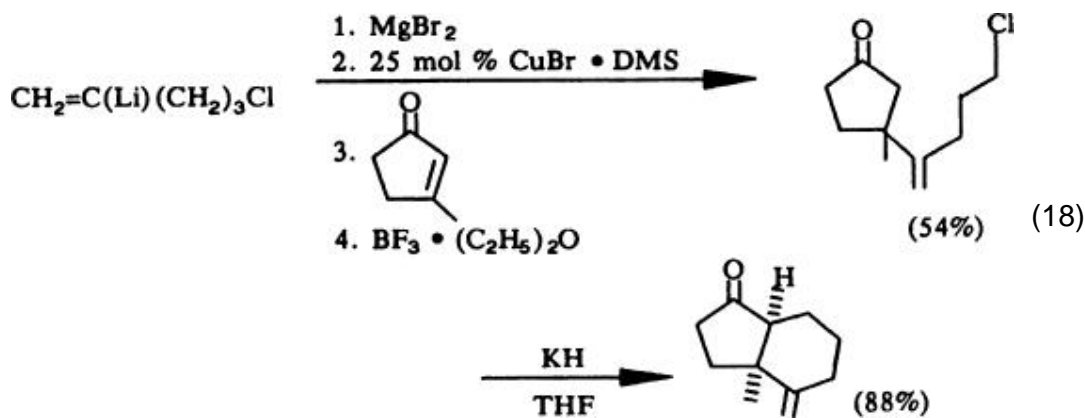
this case! Use of a stoichiometric dialkylcoppermagnesium halide for conjugate addition gives solely O-alkylation of the conjugate enolate.



Activation of the α , β -unsaturated carbonyl substrate by an additional electron-withdrawing group on the α carbon sometimes renders copper(I) catalysis superfluous (Eq. 17). (80)



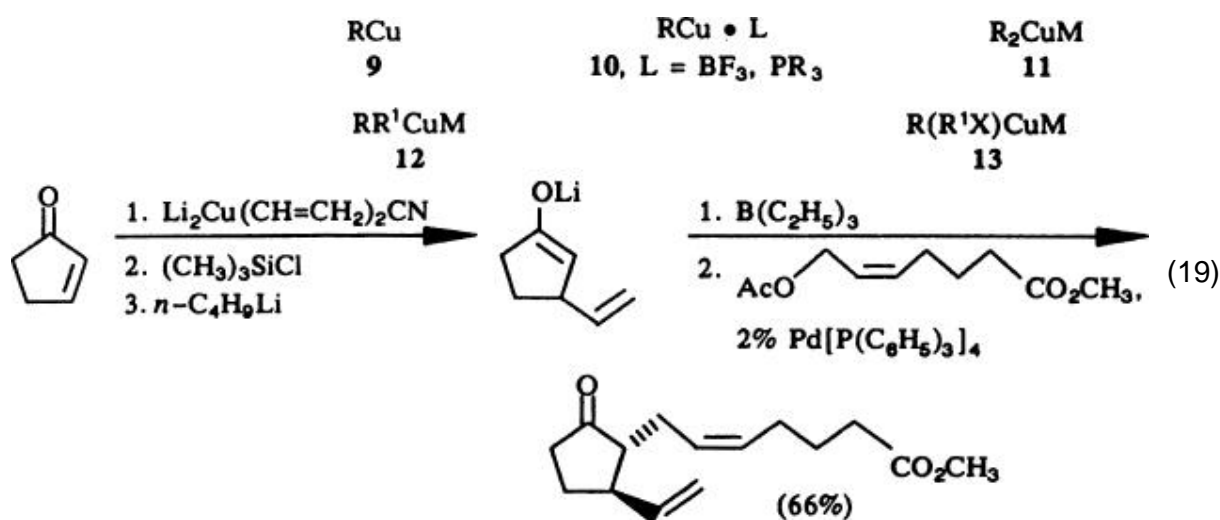
Lewis acids promote 1,4 addition to substrates that are sluggish or nonreactive to copper(I) catalysis alone; (81) methylenecyclohexane annulation of 2-cycloalkenones proceeds in reasonable yields when one equivalent of boron trifluoride etherate is used in addition to copper(I) bromide (Eq. 18). (82)



4.1.1.2. Stoichiometric Organocopper Reagents

A variety of organocopper reagents have found use as efficient nucleophiles to initiate tandem vicinal difunctionalizations of α , β -unsaturated carbonyl substrates, in spite of the fact that one type of organocopper compound may display chemical behavior very different from that of another. Organocopper reagents that begin successful difunctionalization sequences by conjugate addition include: the alkylcopper(I) reagents **9** and **10**, with and without ligating agents that may be essential to their reactivity; dialkylcopper(I) metal reagents **11**, typically generated from Grignard or organolithium reagents and often

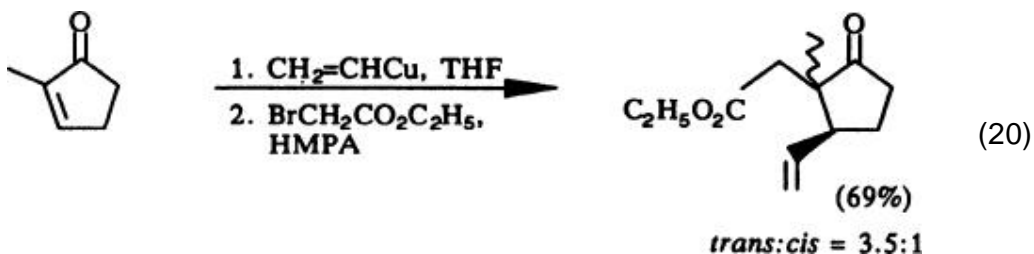
referred to as homocuprates; dialkylcopper(I) metal reagents **12**, generated similarly and referred to as mixed homocuprates, and alkyl(alkylhetero)copper(I) metal reagents **13**, usually prepared from an alkyl metal and the appropriate copper(I) salt and referred to as heterocuprates. The promising “higher-order” complex organocopper reagents (**83**) so far have proven to be unsuitable for use in direct intermolecular tandem difunctionalization reactions (**84**, **85**) but can be applied via a conjugate enolate trapping–enolate regeneration indirect sequence (**86**) (Eq. **19**). Intramolecular alkylation of conjugate enolates occurs upon the addition of cyanodialkylcopper(I) dilithium reagents to α , β -unsaturated esters. (**87**) Undoubtedly, these reagents will be further utilized in difunctionalization schemes.



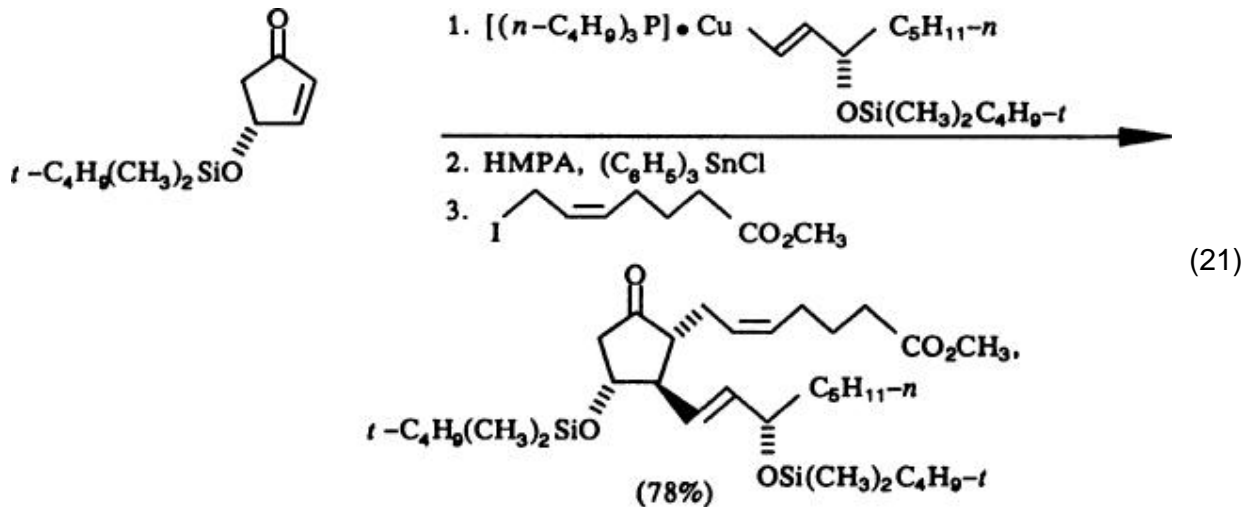
4.1.1.3.1. Organocopper(I) Reagents

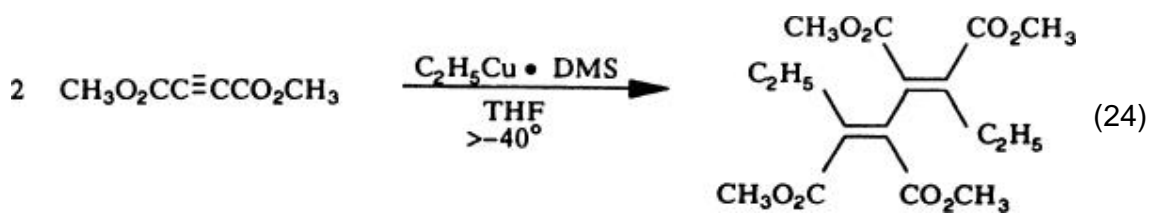
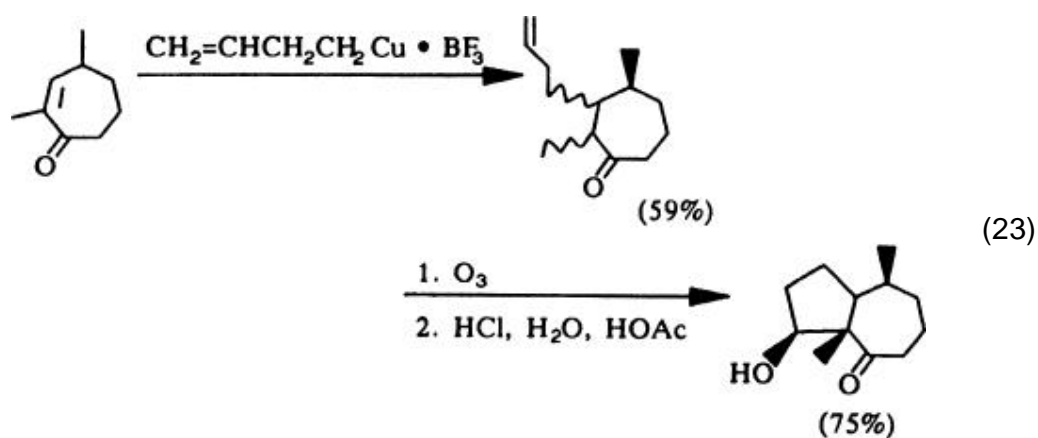
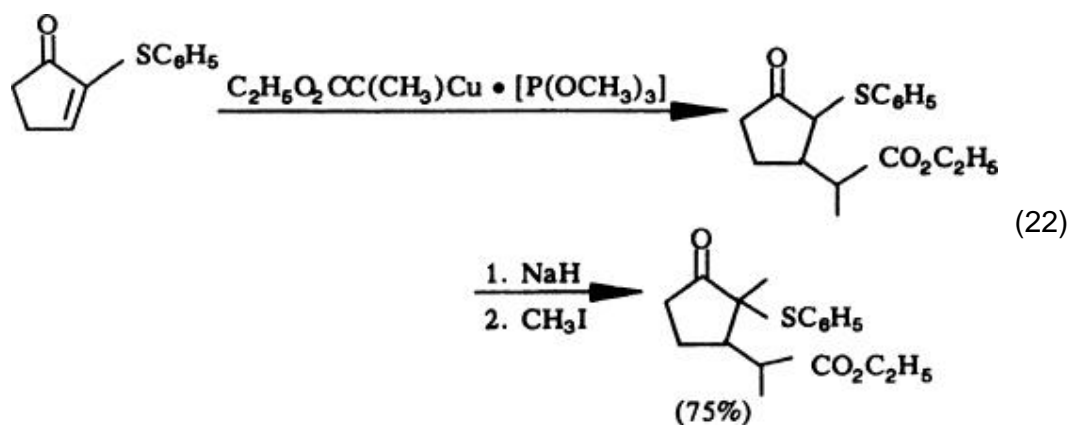
Simple organocopper reagents are almost always less reactive than the corresponding cuprates. This order of reactivity allows the execution of highly successful tandem vicinal dialkylations with cuprate reagents. The conjugate enolate is sufficiently more reactive than the organocopper byproduct so that competition between the two for the α -functionalizing electrophile normally is not significant. A comparative lack of reactivity in conjugate addition reactions explains the rare use of them as Michael donors in vicinal difunctionalization. Vinylcopper reacts with 2-methyl-2-cyclopentenone in a 1,4 fashion (Eq. **20**), (**88**) but most organocoppers are inert. The relative insolubility of organocopper reagents in diethyl ether or tetrahydrofuran (THF), the typical solvents used for the conjugation addition–enolate alkylation sequence, most certainly contributes to their inertness; methylcopper, for instance, is an insoluble polymer in either solvent.

Solubilization via ligation with organophosphorus or organosulfur ligands clearly activates the organocopper reagents toward conjugate addition. Pioneering work has led to the popularization of trialkylphosphines as ligands (Eq. 21); (89) other activating reagents include trialkyl phosphites (Eq. 22), (90)



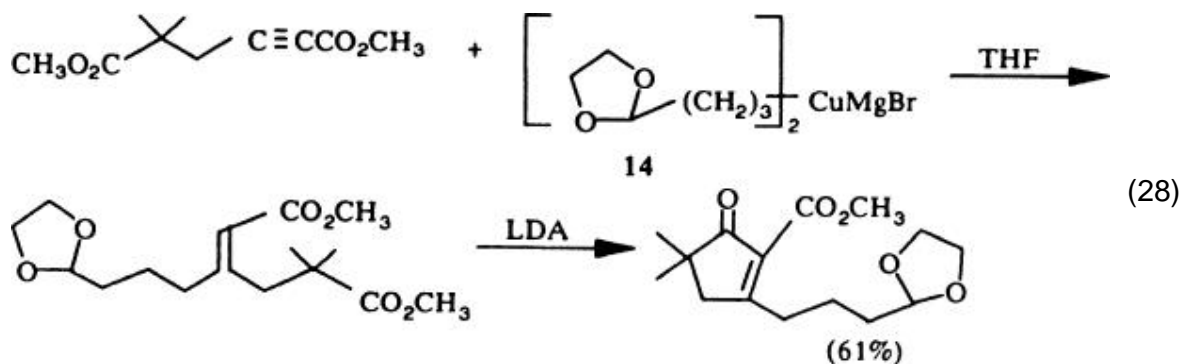
boron trifluoride (Eq. 23), (91, 92) and dimethyl sulfide (DMS; Eq. 24). (93) There is clear advantage in using solubilized organocopper reagents instead of homocuprate reagents when the organometallic precursor is particularly valuable. Only one equivalent of the precursor is necessary to generate one equivalent of the copper species; for one equivalent of homocuprate reagent, two equivalents of the precursor are required. Occasionally, large quantities of solubilizing



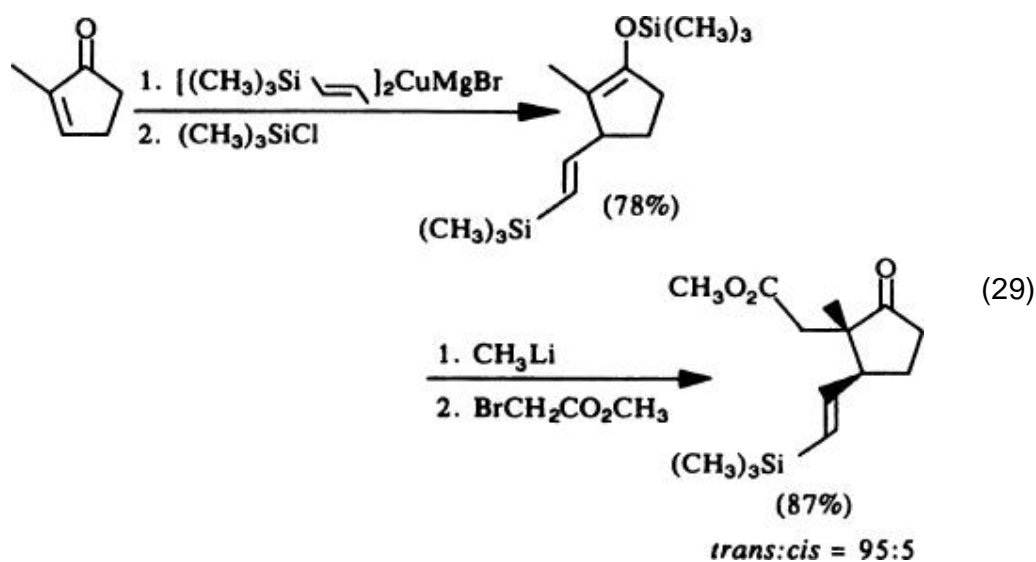


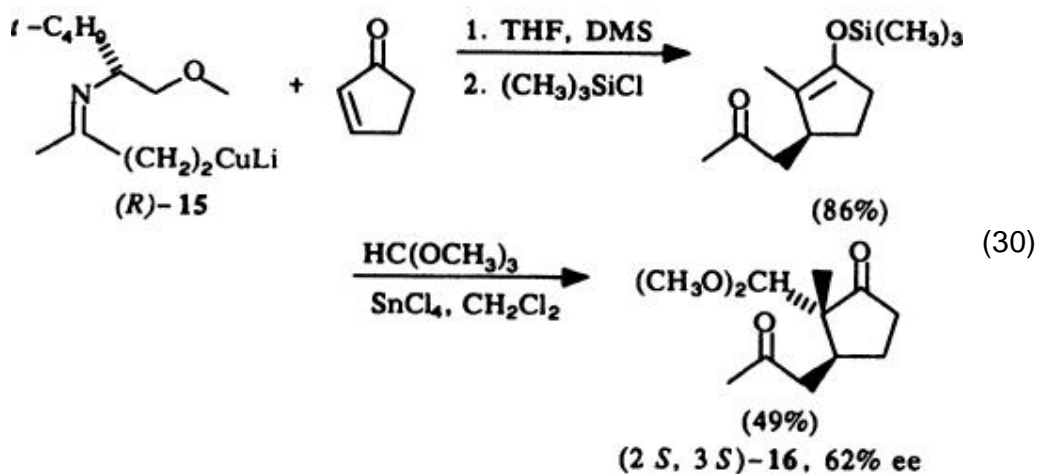
ligand must be used, which causes difficulty in the separation of the products from the reaction mixture; this is frequently observed with trialkylphosphine ligands. Recent studies indicate that organocopper reagents function not only as Michael donor carbanionic synthons but can be extended to function as tin-based anionic synthons as well (Eq. 25). (94, 95)

aryl. No difunctionalization reactions using tertiary dialkylcoppermetal reagents have been reported. (98) Occasionally, these reagents bear additional and even complex functionality. Homocuprate **14**, containing an ethylene acetal moiety, is the Michael donor in a conjugate addition–intramolecular cyclization reaction of acetylenic esters (Eq. 28); (99) bis[(*E*)-trimethylsilylethenyl]coppermagnesium bromide

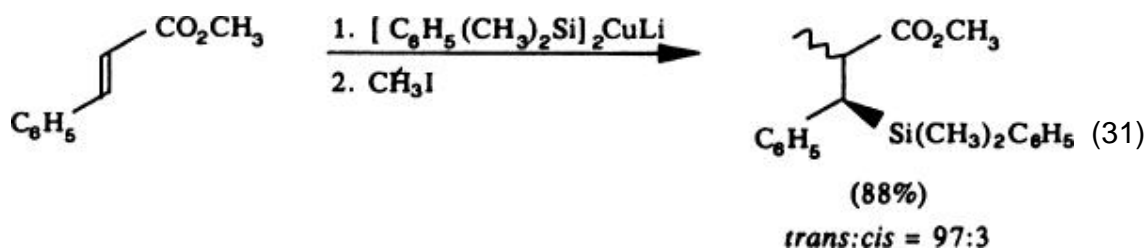


is the β -alkylating agent in a difunctionalization reaction of 2-methyl-2-cyclopentenone (Eq. 29); (100) addition of cuprate (*R*)-**15** to 2-methyl-2-cyclopentenone proceeds with asymmetric induction at the β carbon (Eq. 30) (101) to give (2*S*,3*S*)-**16**. Organosilicon homocuprates

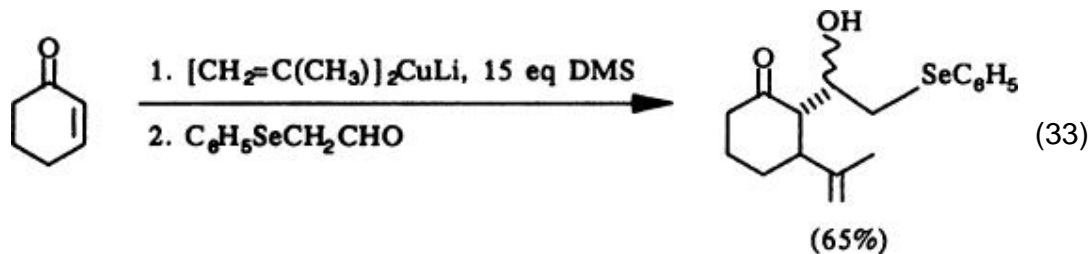
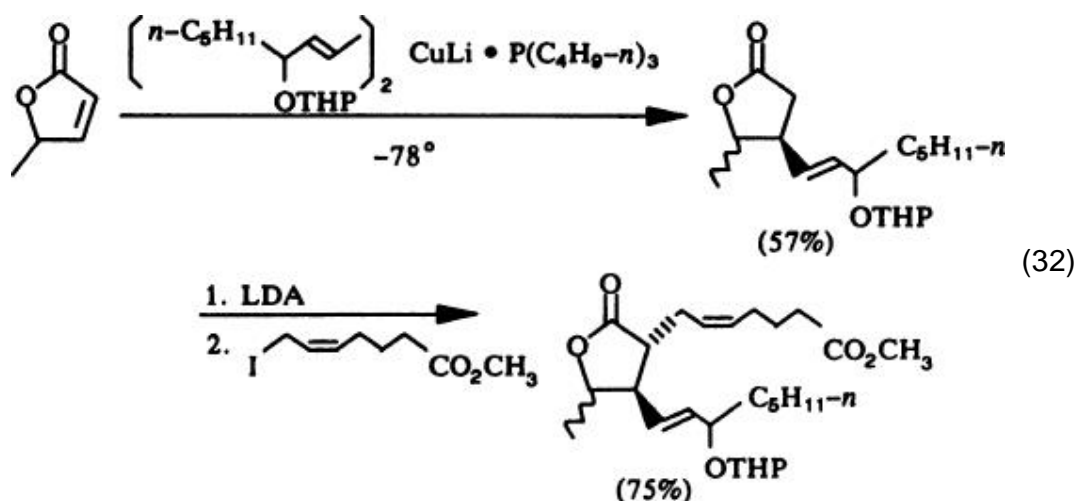




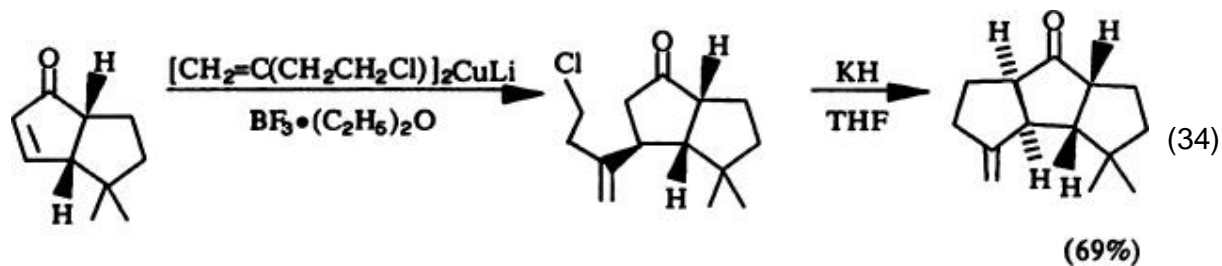
serve as excellent Michael donors (Eq. 31), (102) allowing for reintroduction of unsaturation between the α and β carbons of the carbonyl substrate at a later point in a synthesis via Peterson olefination.



Solubilizing ligands and activating Lewis acids can be used to facilitate difunctionalization reactions using homocuprates, although typically they do not appear to be essential for the reaction to succeed. The ligands simply may be dictated by the desire to use a copper(II)-free source of copper(I) halide that has been purified as its trialkylphosphine or dimethyl sulfide complex (e.g., Eq. 32; 2-tetrahydropyranyl, THP), (103) while in other cases additional ligand is required (Eq. 33). (104) Enhanced yields can result by using boron trifluoride etherate



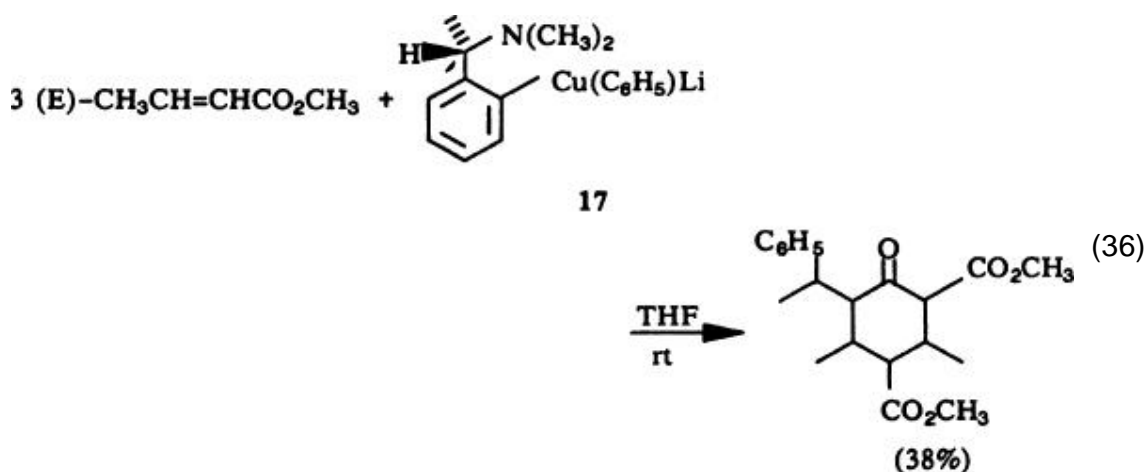
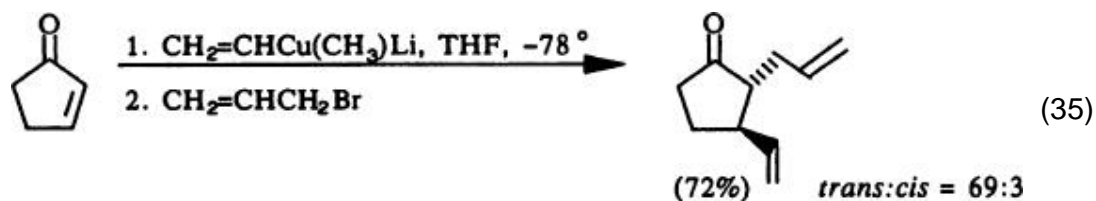
as an activating catalyst for conjugate addition (Eq. 34). (105) Although still untried, the recent observation (52, 106) that trimethylsilyl chloride-modified homocuprates enhance the chemical yields of conjugate additions to α, β -unsaturated ketones should find application in tandem vicinal difunctionalizations via enol ether intermediates.



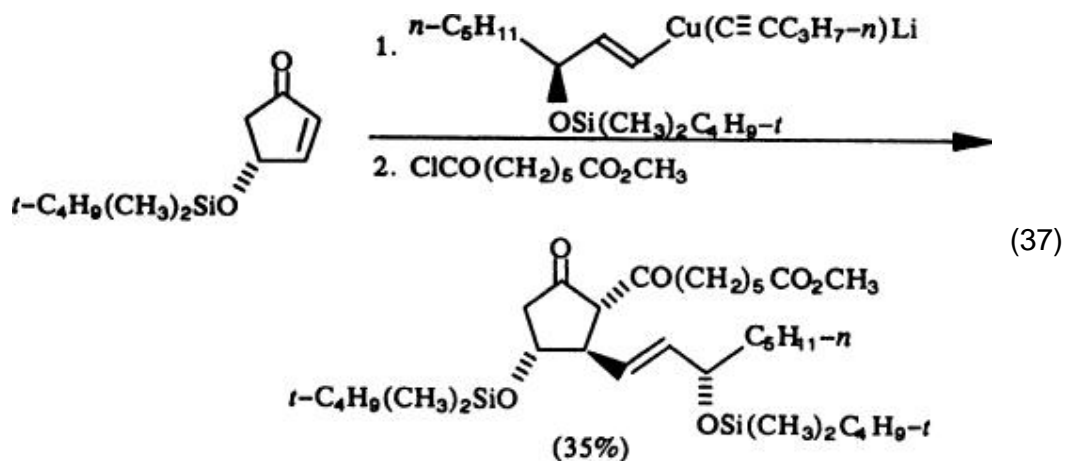
4.1.1.3.3. Mixed Homocuprate Reagents

Unsymmetrical diorganocoppermetal reagents **12** possess two chemically distinct alkyl moieties, only one of which functions as a nucleophile. The two groups usually differ in their formal hybridizations of the carbon atoms bonded to the copper nucleus, and almost invariably the group whose carbon-copper

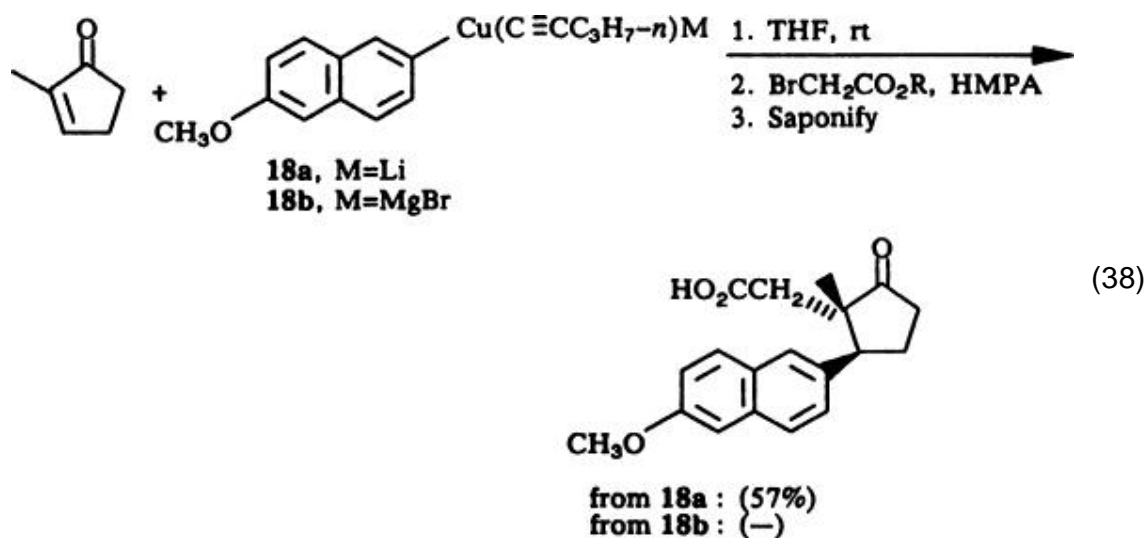
bond contains the lesser *s*-character is transferred to the electrophile, while that with the greater *s*-character is retained. (107) Selectivity of transfer to the electrophile usually is exclusive, and none of the organocopper byproduct is seen to act as a nucleophile. A few exceptions to these generalizations point to the subtle nature of these species: methylvinylcopperlithium preferentially transfers its vinyl moiety in a 1,4 addition reaction with 2-cyclopentenone (Eq. 35), but the selectivity of transfer is solvent-dependent; (108) cuprate **17** transfers its phenyl group exclusively in a trimerization reaction of methyl crotonate (Eq. 36). (109)



Mixed homocuprates typically are generated from an alkynylcopper and one equivalent of an alkyl lithium reagent, although occasionally some other *sp*-hybridized group, such as the cyano group, (110) is used. Among the alkynylcoppers, pentynyl- and hexynylcopper are used most frequently and can be prepared and stored (111) or generated in situ by the addition of an alkynyllithium to a slurry of copper(I) iodide. The 1:1 nucleophile-to-electrophile stoichiometry of the reagents, when compared to the 2:1 stoichiometry of the homocuprates, has made them the preferred reagents in β -chain nucleophilic addition for tandem vicinal difunctionalizations that yield prostanoids (Eq. 37). (112) Alkylalkynylcoppermetal reagents are usually much less reactive than the corresponding homocuprate reagents. (107)

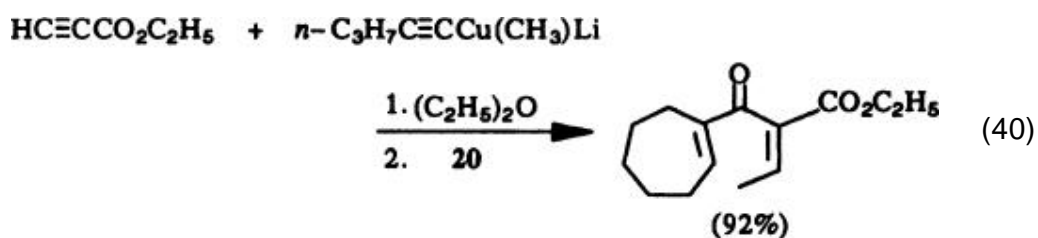
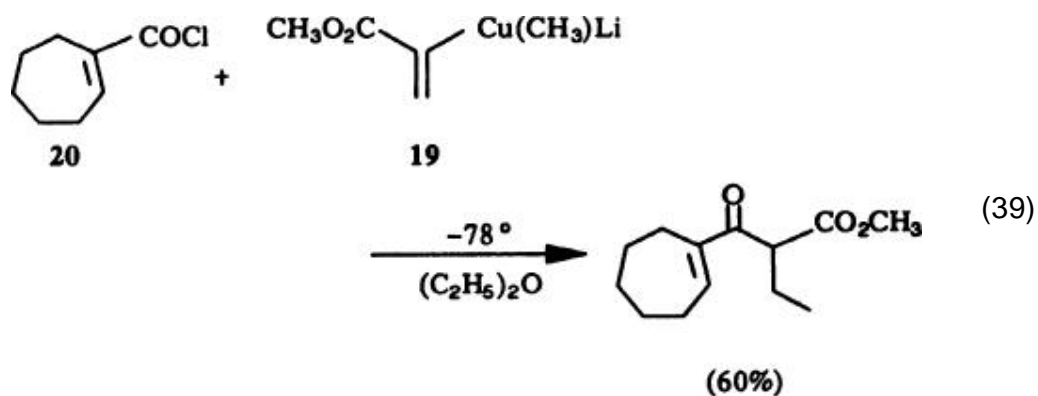


The choice of lithium as counterion versus that of a magnesium halide can have multiple effects. The naphthylcopperlithium reagent **18a** initiates tandem dialkylation of 2-methyl-2-cyclopentenone in 57% yield, (113) whereas use of the corresponding Grignard-derived organocopper reagent **18b** results in a greater amount of β -alkylation, but no net dialkylation, (114) with α -bromoacetates as electrophiles (Eq. 38). The corresponding homocuprate of **18b** fails to undergo conjugate addition with the substrate enone altogether; use of the mixed homocuprate is essential for success of the synthesis.



Mixed homocuprate **19** functions as a novel methyl acrylate synthetic equivalent which undergoes vicinal dialkylation in the reverse order: α -bond formation proceeds by means of organocopper addition to an acid halide **20**,

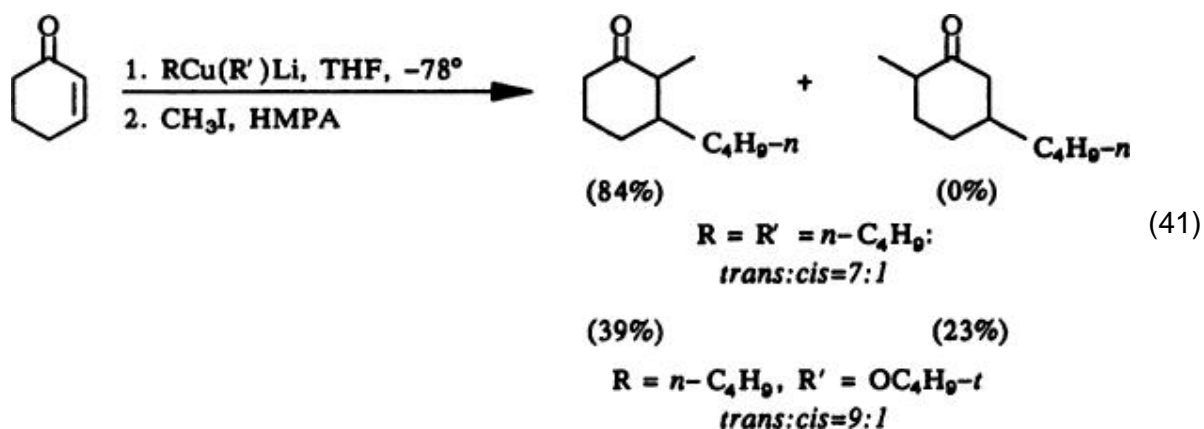
generating an equivalent of methylcopper which then undergoes facile β addition to the highly activated β -keto ester that has been formed in situ (Eq. 39). (110) Introduction of α , β -unsaturation is possible by reversing the order of vicinal dialkylation and starting with ethyl propiolate (Eq. 40). (110)



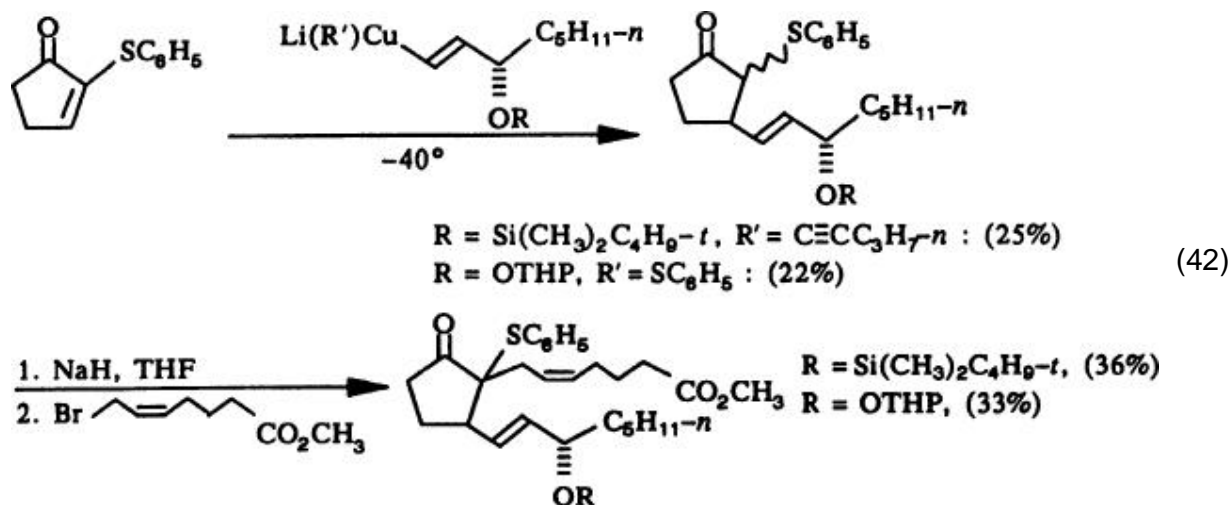
4.1.1.3.4. Heterocuprate Reagents

Much like mixed homocuprates, alkyl(alkylhetero)coppermetal reagents **13** possess only one moiety that acts as a nucleophile. Typically, only the carbon-copper bonded portion is transferred to the electrophile while the heteroatom-copper bonded portion is retained. As a class, the reagents are thermally unstable (115) and must be used at low temperatures; however, they usually are as reactive as the corresponding homocuprate reagents. Reactive, thermally stable heterocuprates have been designed and prepared, (116, 117) but so far have not been used in tandem vicinal functionalization reactions.

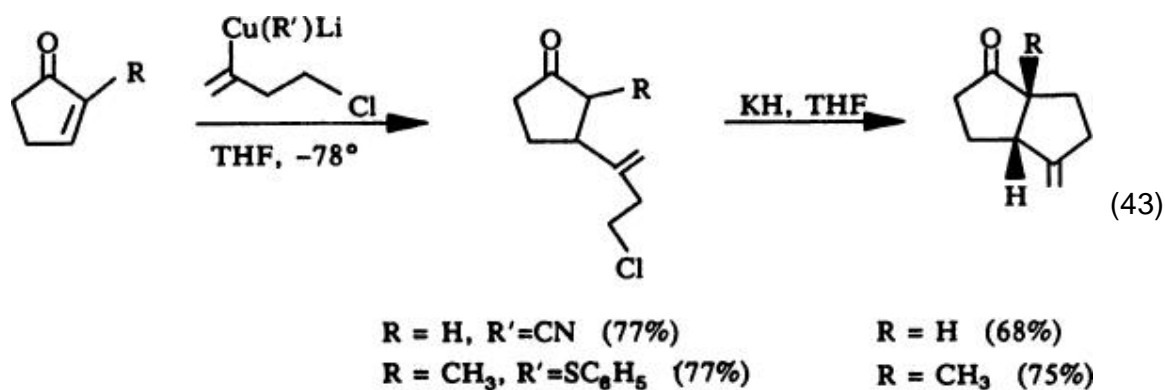
The most common heterocuprate reagents incorporate the phenylthio group and are available by simple treatment of phenylthiocopper with an alkyl lithium reagent at low temperature. Some limited use of alkyl(*tert*-butoxy)-copperlithium reagents made from copper(I) iodide and sequential addition of lithium *tert*-butoxide and an alkyl lithium reagent also has been reported. *n*-Butyl(*tert*-butoxy)copperlithium initiates α , β -dialkylation of 2-cyclohexenone, but is not as efficient a reagent as the simple homocuprate (Eq. 41), (118)



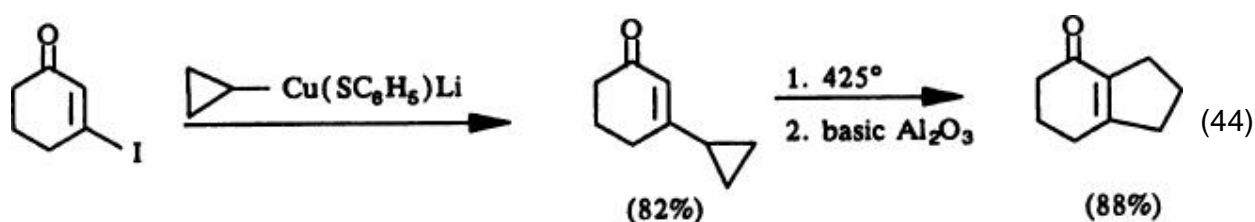
promoting facile equilibration of the conjugate enolate. The heterocuprate does, however, enhance the degree of net *trans* dialkylation of the enone. In comparison of ability to difunctionalize 2-cyclopentenone, neither phenylthio nor pentynyl cuprates offers particular advantage (Eq. 42). (119) A similar



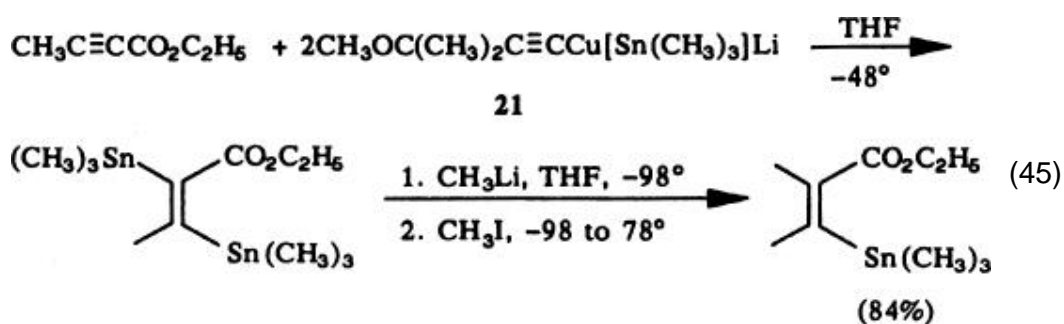
conclusion can be drawn concerning the effectiveness of phenylthio vs. cyano cuprates in the β -alkylation–intramolecular α -alkylation of a variety of 2-cycloalkenones (Eq. 43). (120)



Cyclopropyl(phenylthio)copperlithium reagents are exceptionally useful in a conjugate addition–elimination reaction, followed by α -alkylation via a thermal Cope rearrangement (Eq. 44). (121) An unusual instance of transfer of

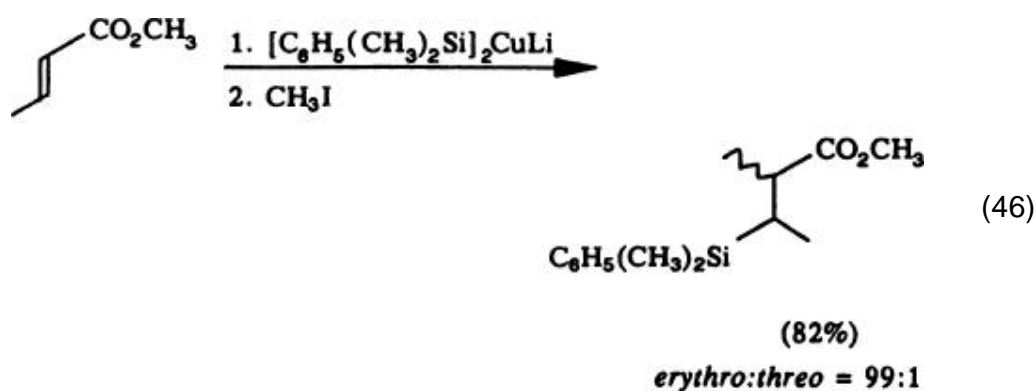


the heteroatom-containing moiety of heterocuprate **21** is illustrated in the conjugate trimethylstannylation of ethyl 2-butynoate (Eq. 45), in which **21** is as effective as the corresponding trimethylstannylcopper reagent. (94)

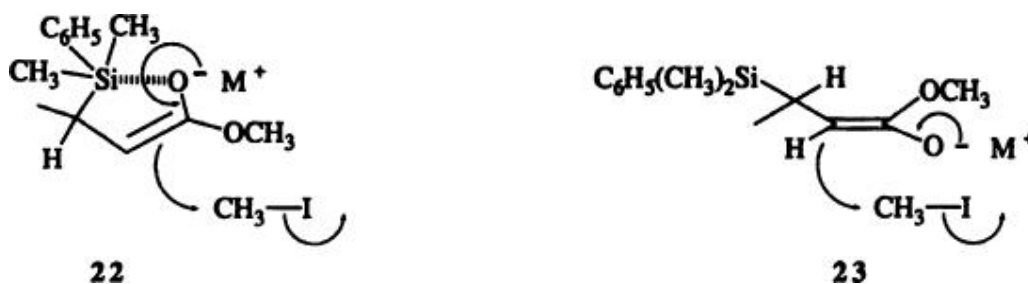


4.1.1.4. Effect of Variation of the R Group Transferred on α -Functionalization
 Trans difunctionalization of α, β -unsaturated carbonyl substrates predominates in nearly all cases and is relatively independent of the size or hybridization state of the nucleophile undergoing 1,4 addition to the substrate. When heteroatom-containing functional groups are present in the Michael

donor, subsequent chelation or coordination may determine the solution structure of the conjugate enolate. Cases where this type of influence on α -functionalization has been observed are rare. The high level of *trans* diastereoselectivity noted (102) when methyl *trans*-crotonate is reacted with phenyldimethylsilylcopperlithium, followed by methyl iodide (Eq. 46), can be envisioned as arising from one of two routes. The conjugate enolate may be chelated to the silyl moiety **22**, the methyl iodide approaching the less hindered face of the cyclic intermediate. Alternatively, the stereoelectronic influences of the lower-energy conformation of the conjugate enolate **23** may direct the electrophile to attach *anti* to the silyl group. Evidence points to the latter; the silyl group does not appear to perturb normal conjugate enolate behavior toward electrophiles. The previously mentioned lithium–arene π -coordination



of the conjugate enolate from addition of diphenylcopperlithium to cyclopentenones (Eq. 8) directs *cis*- α -functionalization. The effect is weak; 2-substituted



cyclopentenones disrupt the coordination, as do cyclohexenones, and the *trans*-dialkylated products predominate. (67)

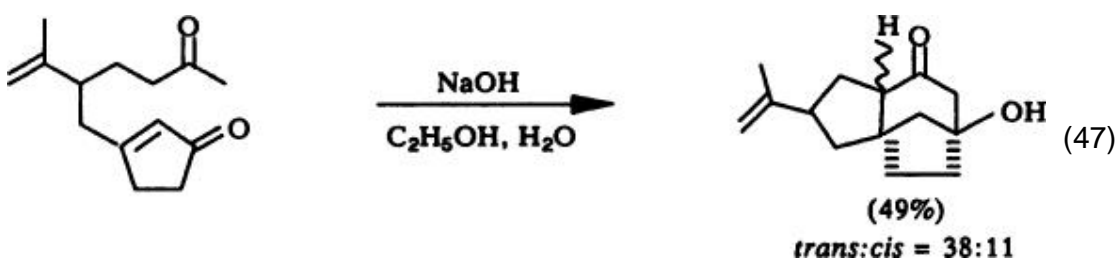
4.2. Other Reagents

4.2.1.1. Stabilized Reagents

Carbanionic nucleophiles can be made into effective reagents for conjugate addition reactions by “softening” their Lewis base characteristics. Appending resonance and/or inductive stabilizing groups to carbanions renders them excellent Michael donors.

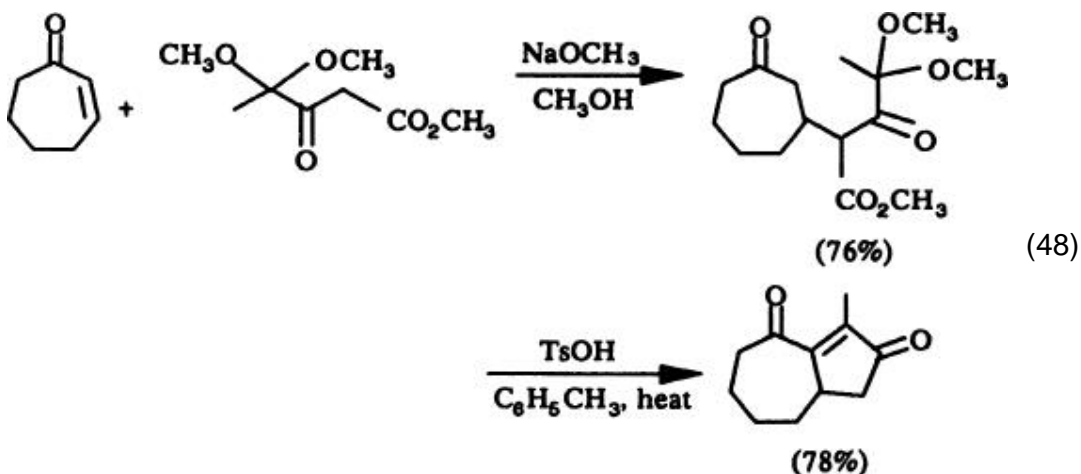
4.2.1.1.1. Enolate Reagents

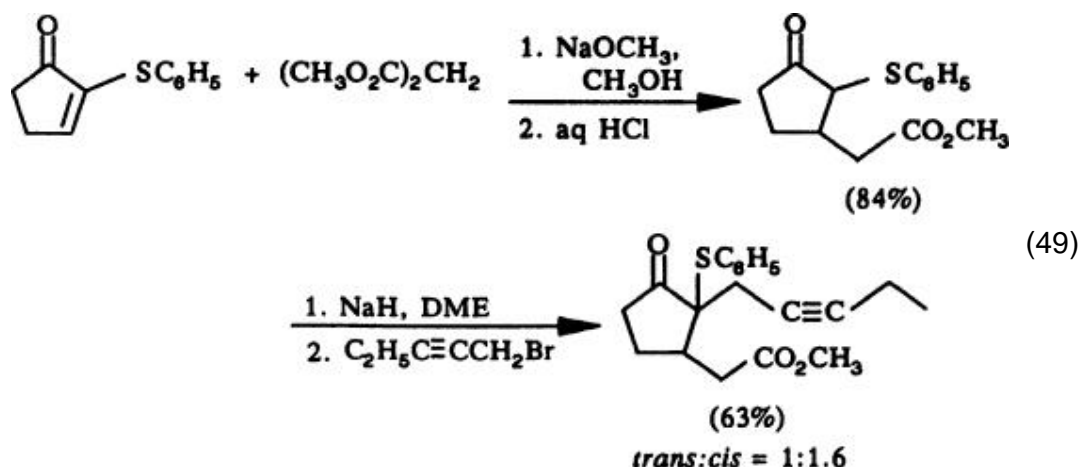
Although often used as a generic descriptor for 1,4 or conjugate addition, Michael addition refers to the observed 1,4 addition of an enolate anion to an α, β -unsaturated carbonyl substrate resulting in a 1,5-dione. (122) The reaction is tightly linked to tandem vicinal difunctionalization, being responsible for the “secondary” products of Grignard reactions and the first examples of the difunctionalization sequence, as previously discussed. Classical Michael addition reactions are conducted in protic media. To compete effectively with proton capture for the enolate, the α -functionalizing reagent needs to be intramolecular in nature (Eq. 47); (123) alternatively, the Michael adduct can be isolated and α -functionalized under a different set of



reaction conditions, for example, an acid-catalyzed aldol reaction (Eq. 48) (124) or alkylation of a regioselectively generated conjugate enolate (Eq. 49; 1,2-dimethoxyethane, DME). (125)

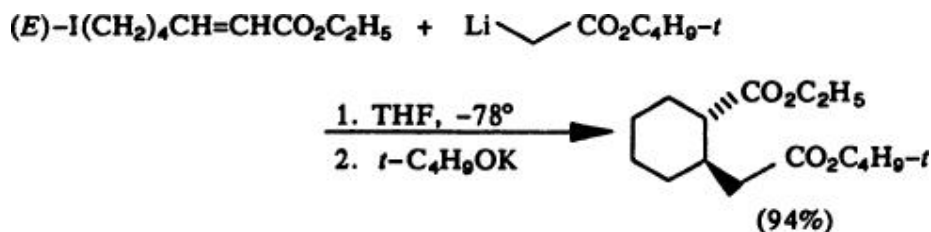
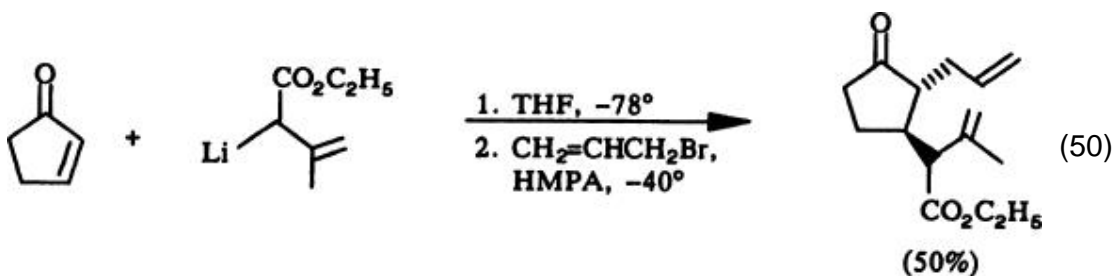
Enolate-based tandem vicinal difunctionalization in protic solvents suffers from the typical disadvantages of self-condensation (which occasionally may be of use), (126) side reactions of the bases (usually alkoxides) used to catalyze the reactions, and “retro-Michael” reactions that occur at elevated temperatures due to the reversibility of the reaction. Not surprisingly, conjugate-addition–alkylation





sequences in aprotic media have supplanted the Michael reaction.

A prototype reaction demonstrates the ease with which difunctionalization occurs at low temperature: 2-cyclopentenone undergoes 1,4 addition by an ester enolate; the conjugate enolate then is trapped with allyl bromide (Eq. 50). (127) Intramolecular trapping of conjugate enolates also is possible, resulting in cyclization reactions often referred to as Michael Ring Closure or MIRC (128) reactions (Eq. 51). (129) The most efficient ester enolates possess α -heteroatom substituents, examples of which include arylthio, alkylthio, halo, methyldiphenylsilyl, arylsulfonyl, (130) and alkoxy groups. The Michael donor need not

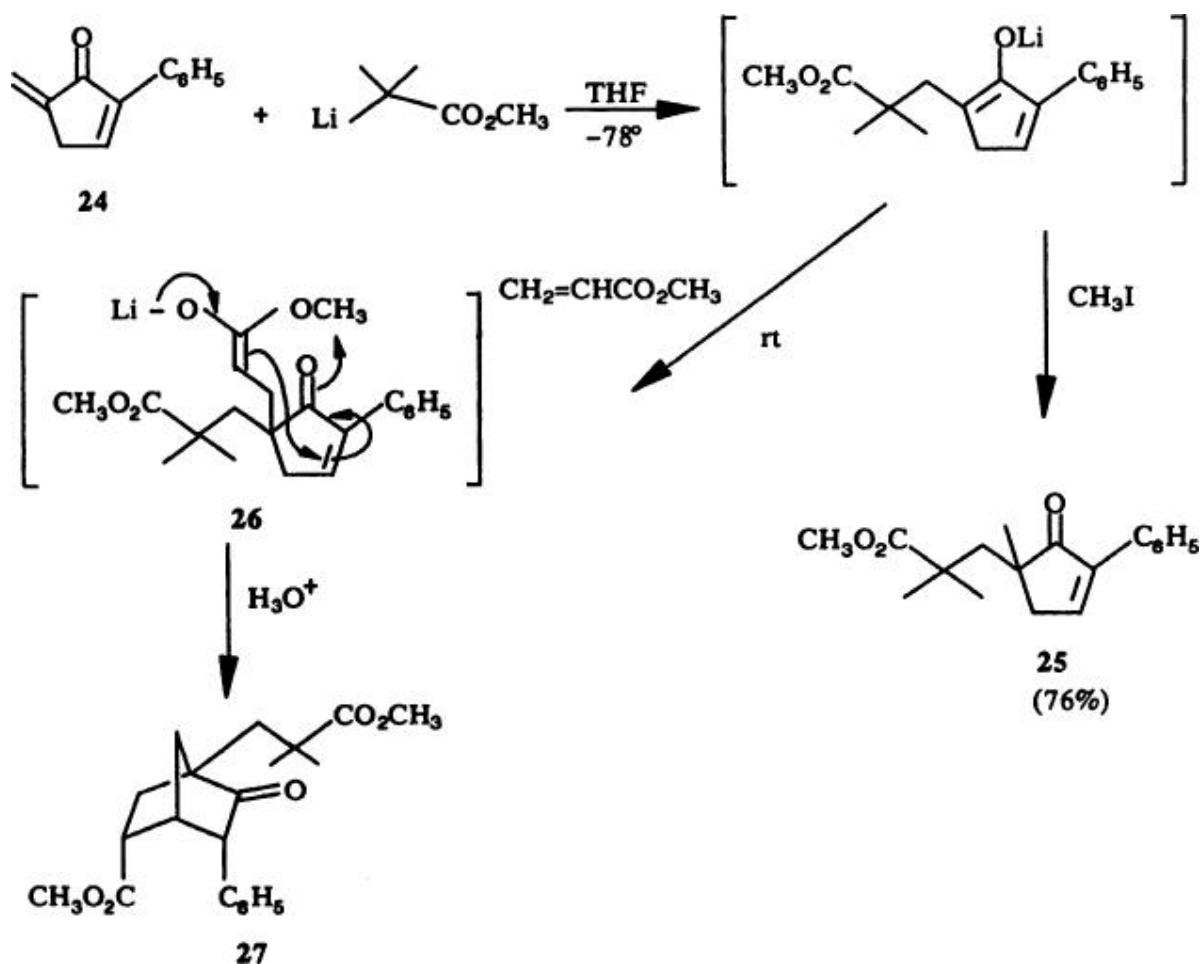


be generated directly from an ester and a hindered non-nucleophilic base, but

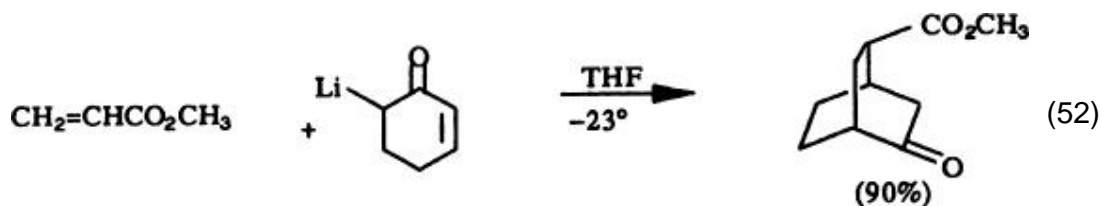
can be generated instead from an enolate equivalent, the most popular being a silyl enol ether. Methyl lithium, (4) fluoride-mediated, (131, 132) or trityl perchlorate-catalyzed (133, 134) enol ether cleavages are effective methods for Michael donor formation in tandem vicinal difunctionalizations and in some cases may produce better yields of desired products.

An interesting modification of the Michael-addition– α -functionalization reaction involves the use of a second Michael acceptor as the electrophilic reagent for α -functionalization of the conjugate enolate. Ketone **24**, by way of example, undergoes conjugate addition of the lithium enolate of methyl 2-methylpropanoate; the resultant conjugate enolate then is C-methylated using methyl iodide to provide the ketone **25** (Scheme 8). (135) When methyl acrylate is substituted for methyl iodide, α -functionalization generates a new ester enolate, **26**, with net tandem vicinal difunctionalization of substrate **24**. The new enolate now undergoes yet a *third* conjugate addition reaction with the 2-phenyl-2-cyclopentenone moiety still present in the molecule from the original substrate **24**, forming norbornanone **27** in 40% overall yield, or in 74% chemical yield per carbon–carbon bond formed in the reaction. (136) One-pot, three carbon–carbon bond-forming, two-component double tandem vicinal difunctionalization reactions with subsequent ring closure belong to a class of reactions called Michael–Michael Ring Closure (MIMIRC) or Sequential Michael Ring Closure (SMIRC) reactions. (137) These controlled anionic codimerization and cotrimerization reactions can proceed in high yields and with excellent control of stereochemistry, generating complex polycyclic structures.

Scheme 8.



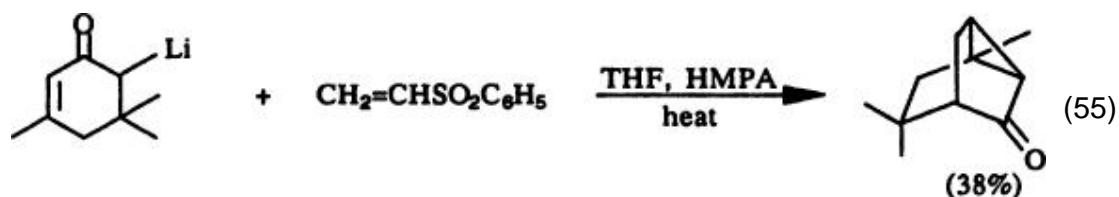
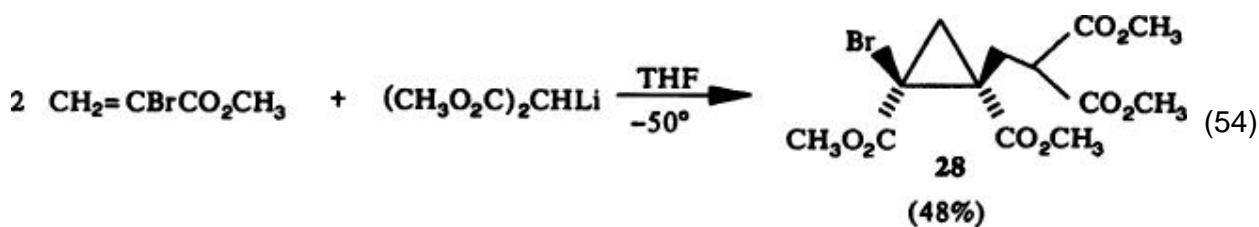
Most MIRC and MIMIRC reaction sequences are initiated by ketone enolates, as opposed to ester enolates. The kinetic enolate of 2-cyclohexenone undergoes 1,4 addition with methyl acrylate; the conjugate enolate then performs a second intramolecular Michael addition with concomitant ring formation to yield the bornanone ring system (Eq. 52). (138, 139) An intramolecular version, where both initial Michael donor and acceptor are contained in the

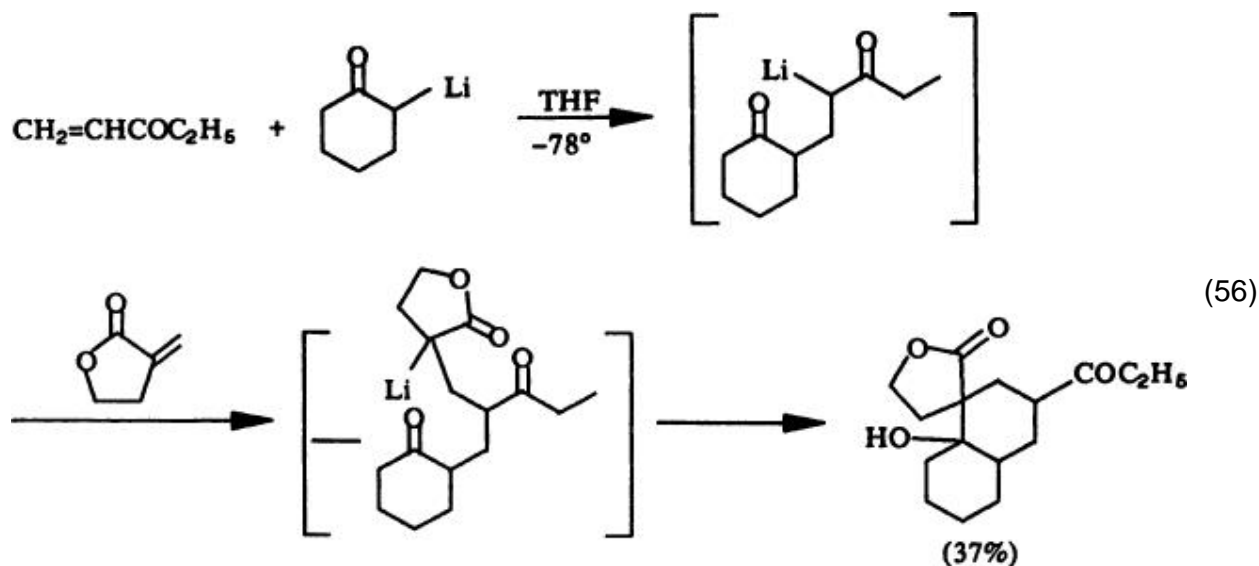


same molecule, has been reported; (140) two carbon-carbon bonds and two rings are formed with complete control of stereochemistry (Eq. 53; lithium hexamethyldisilazide, LiHMDS).

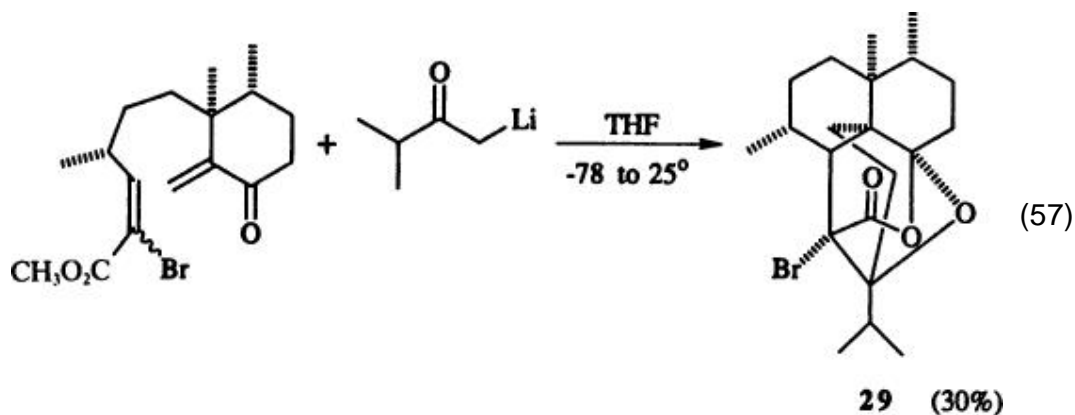


Both inter- and intramolecular cyclopropanation reactions are possible using MIMIRC methodology: a malonate-initiated dimerization of methyl α -bromoacrylate affords the cyclopropane **28** (Eq. 54); (141) the tricyclo[2.1.1.0]-octane ring system is produced in the reaction of phenyl vinyl sulfone with the kinetic enolate of isophorone (Eq. 55) (142) The production of spiro compounds also is possible (Eq. 56). (143) A recent synthesis of epiflavinine uses a cascade of sequential Michael reactions, ketalization, and esterification all in



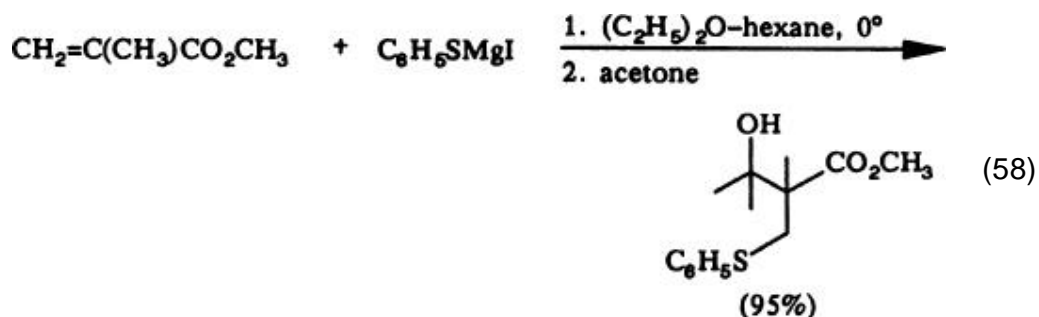


an intramolecular sense to afford the complex polycyclic system **29** (Eq. 57). (144) The MIMIRC methodology affords the advantages of convergence and stereocontrol, boding well for its application in total synthesis.

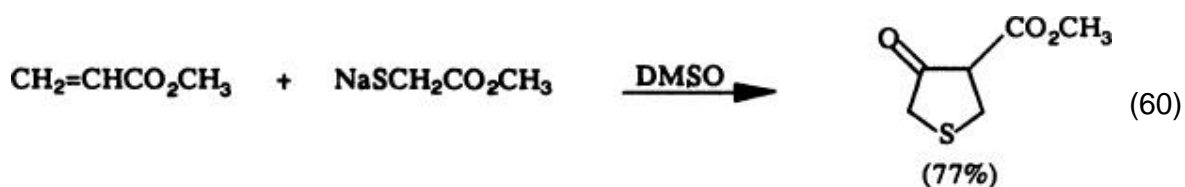
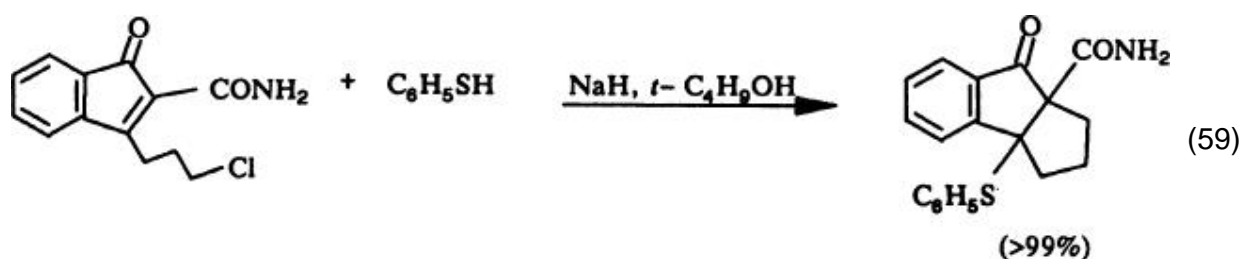


4.2.1.1.2. Sulfur-Stabilized Reagents

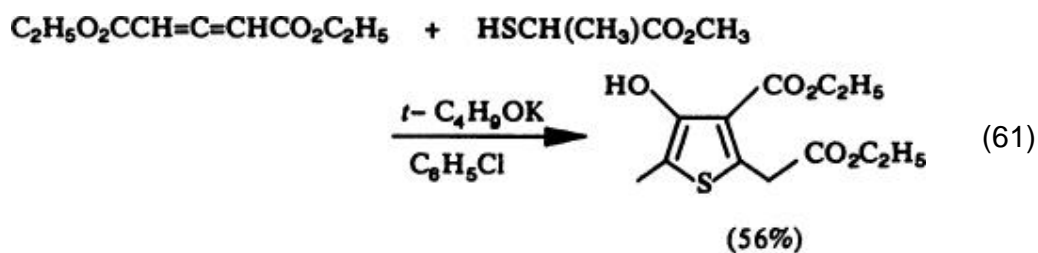
Mercaptide anions are good Michael donors in tandem vicinal difunctionalization reactions. Esters and ketones undergo tandem phenylthiolate conjugate addition–aldol reactions (145) to give β -phenylthio- β -hydroxy esters and ketones (Eq. 58). A fully formed thiophenoxide salt may be used as the initial nucleophilic reagent, or the reaction may be performed with base catalysis. (146) Mercaptides have found particular use in investigations of the scope of MIRC-type reactions. The α -alkylating fragment



for the reaction sequence can be part of the Michael acceptor (Eq. 59) (147) or part of the Michael donor (Eq. 60; dimethyl sulfoxide, DMSO). (148) The latter

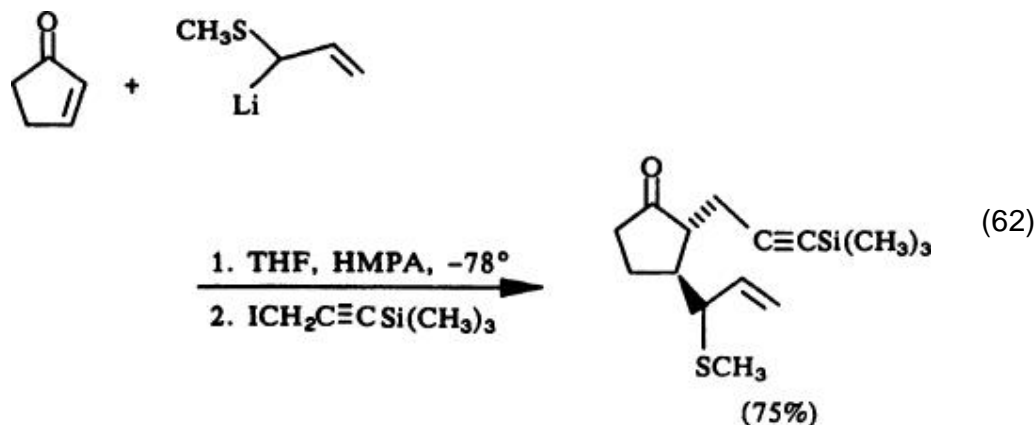


approach recently has been used in a synthesis of regiospecifically substituted thiophenes from allene diesters (Eq. 61). (149)

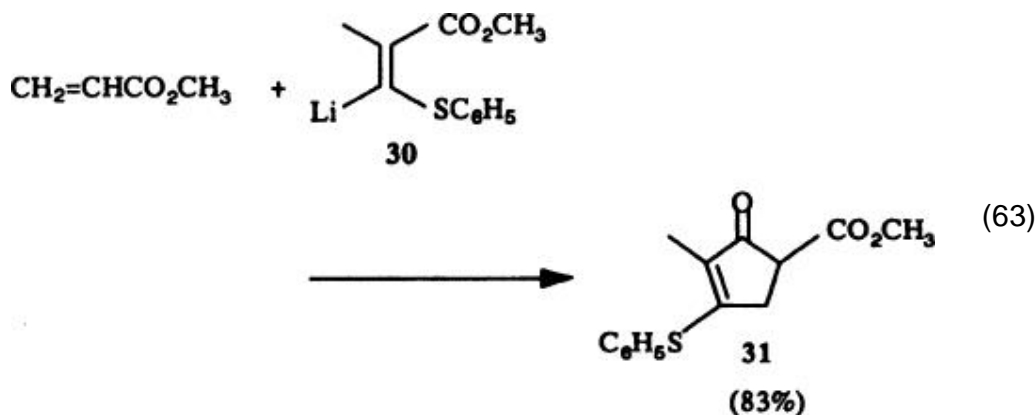


The stabilizing effect of a sulfur atom upon an adjacent carbanionic center permits the straightforward synthesis of 4-alkylthioketones by means of tandem difunctionalization. Ambident allylic anions react so that

carbon–carbon bond formation occurs exclusively (150) from the α carbon (Eq. 62). (151) Arylsulfinyl (152) and arylsulfonyl (153) groups behave in similar fashion and in all cases yields of the conjugate enolates normally are good. In contrast, an example of an arylsulfinyl-stabilized allylic anion that undergoes exclusive carbon–carbon bond formation with 2-cyclopentenone from its γ carbon recently has been described. (154) This regiospecific mode of addition also is exhibited by an analogous diphenylphosphinyl-stabilized allylic anion. (155) Stabilization via sulfur

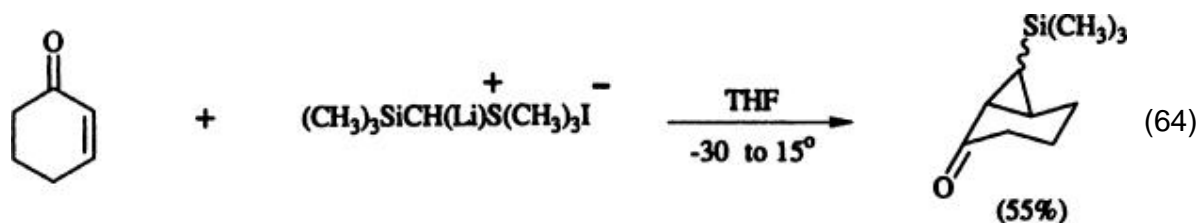


also finds synthetic utility in the formation of vinylic anions that will function as Michael donors. In a total synthesis of (\pm)-methylenomycin A, (156) the regiospecifically metalated methacrylate **30** undergoes a conjugate addition reaction with methyl acrylate; α -functionalization by Dieckmann cyclization results in formation of cyclopentenone **31** (Eq. 63).

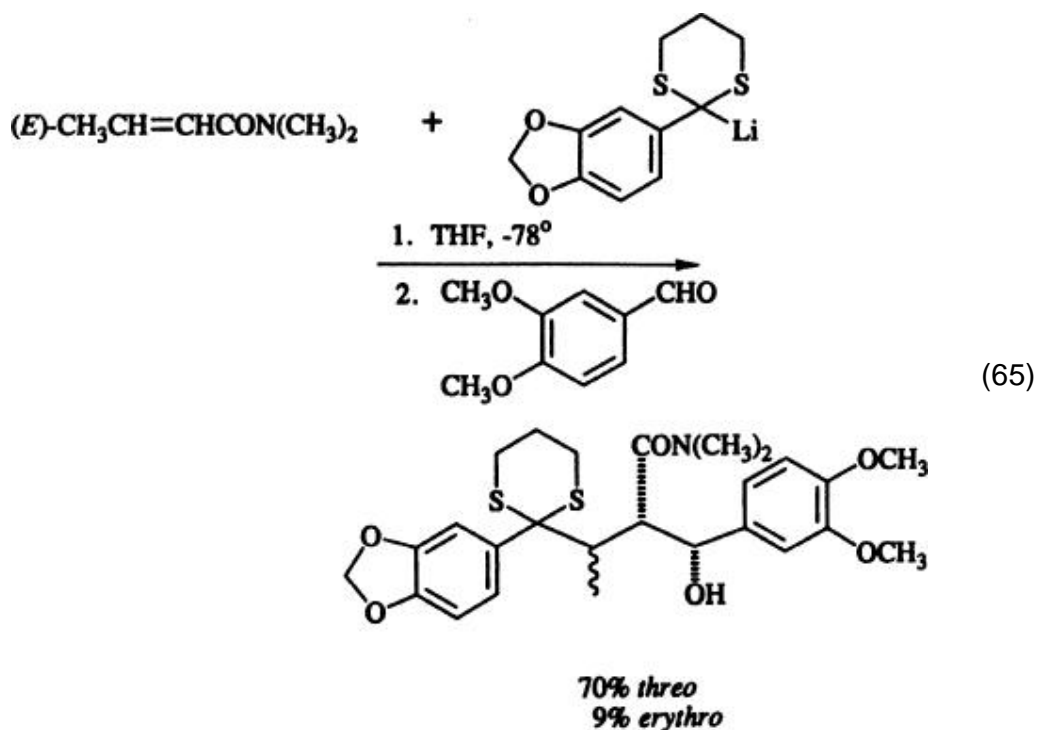


It is possible to develop reagents wherein the stabilizing organosulfur substituent serves a dual role. Metalation of trimethylsilylmethyltrimethylsulfonium iodide provides an ylide that undergoes

conjugate addition to enones. The trimethylsulfonium moiety then functions as a leaving group when intramolecular attack of the conjugate enolate occurs, resulting in net cyclopropanation (Eq. 64). (157)



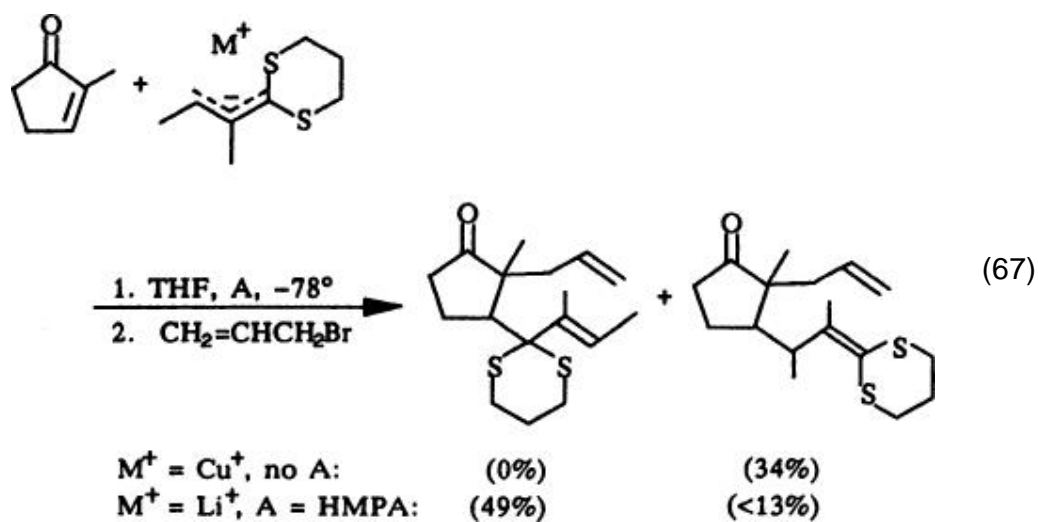
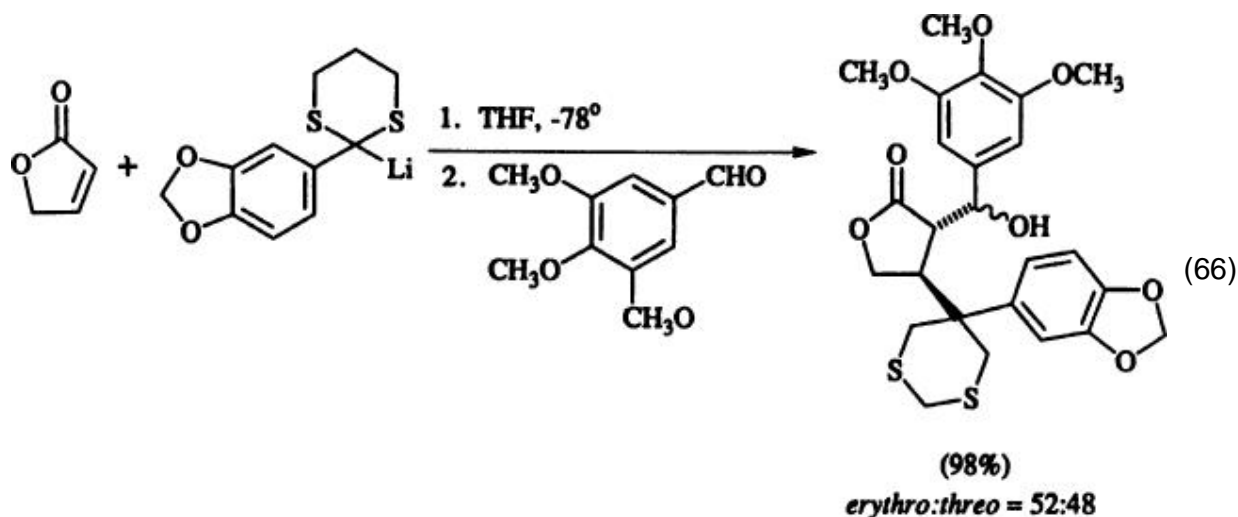
Dialkylthiomethanes act as acyl anion equivalents when used in a tandem vicinal difunctionalization and can provide entry into substituted 1,4-diketones. Lithiated dithianes undergo conjugate addition–aldol condensations with *N,N*-dimethylcrotonamides with considerable stereoselectivity (Eq. 65). (158) A number of lignan antibiotics such as (\pm)-podorhizol (159) have thereby



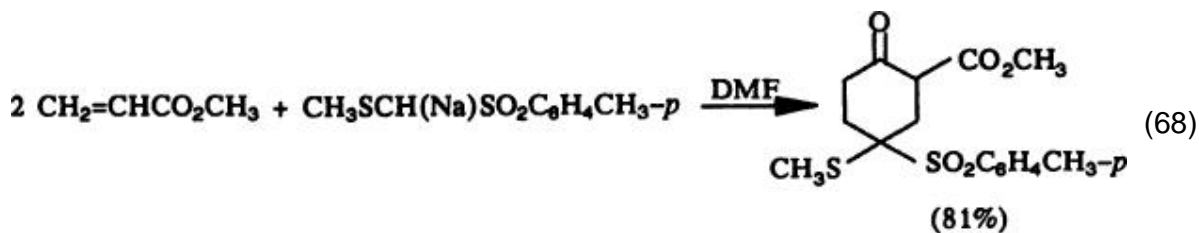
been prepared in a highly convergent manner using similar strategies (160-163) (Eq. 66).

Ambident dithianylidene anions act as Michael donors for conjugate additions to enones. An α -1,4 or γ -1,4 addition mode may be achieved by altering the

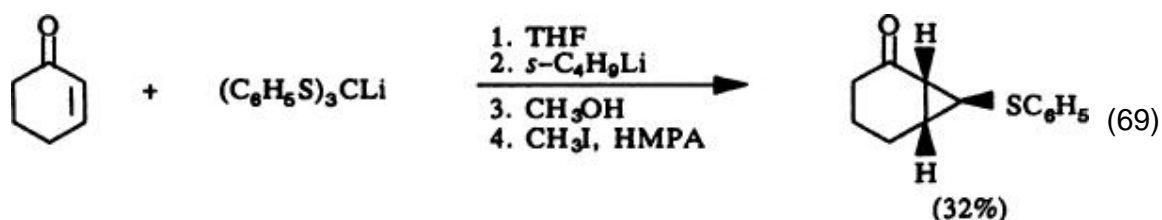
counterion (Li^+ vs. Cu^+) or by use of HMPA as a solvent adjuvant (Eq. 67). (164)
 Either of the sulfur atoms in a dialkylthiomethane reagent can be oxidized; the resultant alkylthiomethyl sulfoxides (165) and sulfones (166) also



are efficient Michael donors. The sodium salt of methylthiomethyl *p*-toluyl sulfone initiates a MIMIRC-type reaction with two molecules of acrylate, resulting in the synthesis of a β -ketoester (Eq. 68).

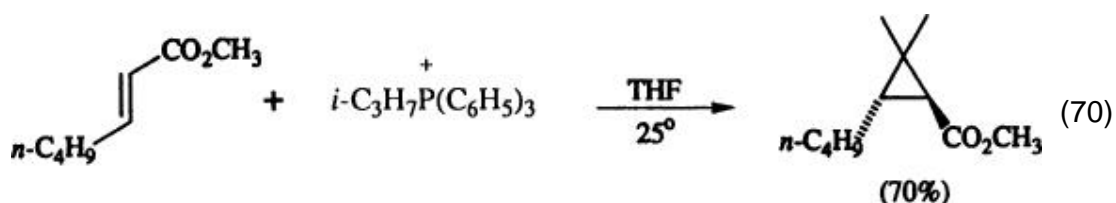


Orthothioformates (167, 168) and their analogs (169) have been used only recently in tandem difunctionalization strategies. In a particularly interesting example, the nucleophilic carbon atom of triphenylthiomethyl lithium undergoes umpolung in situ after conjugate addition to 2-cyclohexenone, functioning as the α -alkylating agent of the conjugate enolate in a MIRC-type cyclopropanation (Eq. 69). (167)

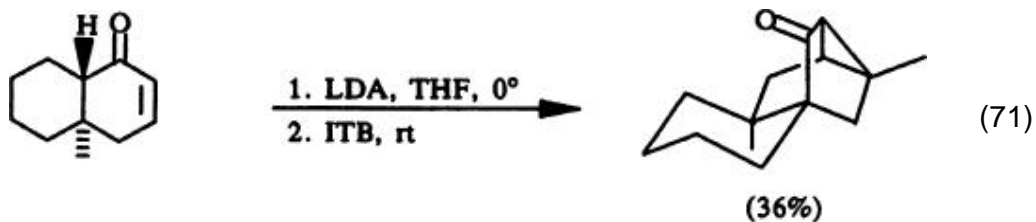


4.2.1.1.3. Phosphorus Ylide Reagents

Like the sulfonium ylides previously discussed (Eq. 64), phosphonium ylides can be employed as cyclopropanating reagents for unsaturated ketones and esters by means of β -conjugate addition— α -intramolecular alkylation. (170-172) Even hindered ylides undergo the reaction; the ylide generated from isopropyltriphenylphosphonium halide undergoes reaction with α , β -unsaturated esters to yield *gem*-dimethylcyclopropanes (Eq. 70). (173) Intramolecular cyclopropanation is observed when a

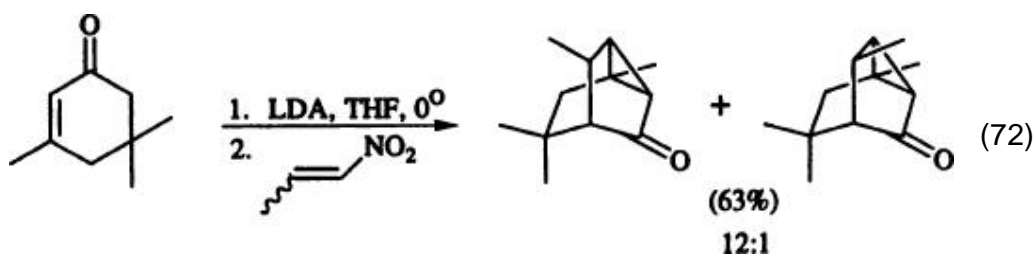


phosphonium ylide is generated during a MIMIRC sequence (Eq. 55). Commonly used for this purpose are phosphonium salts bearing a vinyl substituent, including vinyltriphenylphosphonium bromide (VTB, Schweitzer's reagent) (174, 175) and isopropenyltriphenylphosphonium bromide (ITB, Eq. 71). (176)

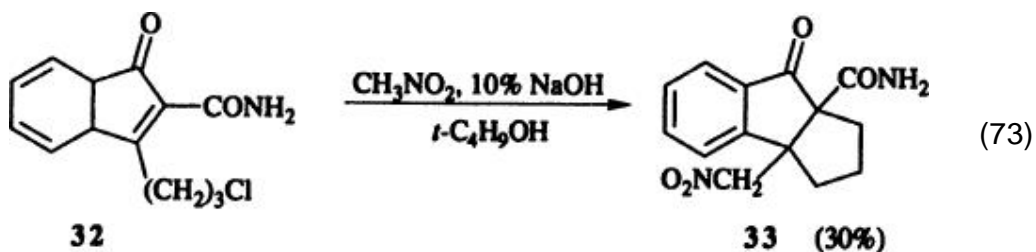


4.2.1.1.4. Nitroalkanes

Nitroalkanes also can serve as cyclopropanating reagents for α , β -unsaturated esters that are activated for Michael additions by α -substitution with an electron-withdrawing group. (177, 178) Similar to the phosphorus ylide employed in Eq. 70, 2-nitropropane functions as a Michael donor– α -alkylating agent for an α , β -unsaturated α -cyanoester in protic solvents using potassium carbonate as base to give *gem*-dimethylcyclopropanes in good yields and singular stereochemistry. (177) 1-Nitroalkenes act as superior VTB-like equivalents in MIMIRC reactions; isolated yields of the products typically are high (Eq. 72). (179) Nitromethane adds to β -ketoamide **32**. Subsequent



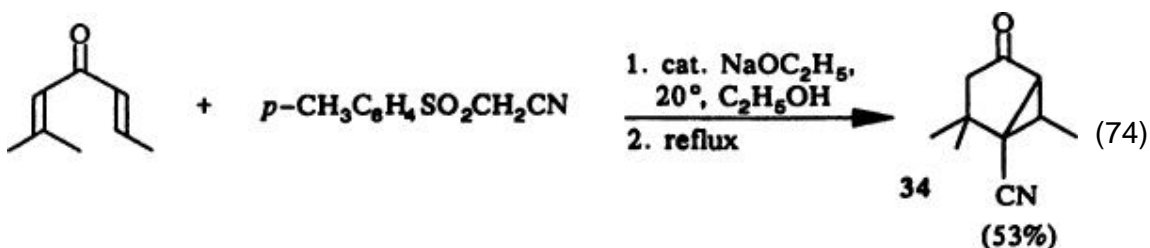
intramolecular alkylation occurs in only one of two possible fashions; no cyclopropane is produced, and only cyclopentane **33** is observed (Eq. 73). (147)



In a MIRC-type sequence using 5-nitro-2-pentanone as a Michael donor to 2-cyclopentenone, no cyclopropane products are noted, and normal ring closure via an aldol reaction results in the expected cyclohexane. (180)

4.2.1.1.5. Other Reagents

The cyanide anion, both in protic (147) and aprotic (181, 182) solvents, can be used in MIRC-type reactions. Benzylic anions stabilized by the cyano group are excellent Michael donors (183-185) and, like their enolate anion equivalents, provide the opportunity for further elaboration of the 1,5-difunctional product from the tandem difunctionalization reaction. (186, 187) The reagent *p*-toluenesulfonylacetonitrile serves three purposes in the preparation of a bicyclo[3.1.0]hexanone 34; it is a double Michael donor to a divinylketone to form a cyclohexanone; γ -elimination of the sulfonyl moiety then establishes the ring fusion (Eq. 74). (188)



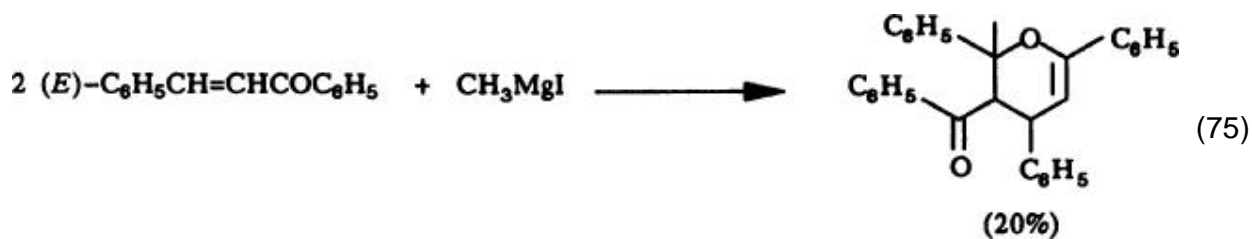
Silyllithium reagents and trimethylsilyl-stabilized benzylic anions (189) can serve as Michael donors. Trimethylsilyllithium is an excellent Michael donor to 2-cyclohexenone: (55) as such, it may have implications to the mechanistic details of the tandem difunctionalization sequence.

4.2.1.2. Unstabilized Reagents

Organometallic reagents that are Lewis bases can be used directly or with a transition metal catalyst to perform conjugate additions, particularly when the unsaturated carbonyl substrate is relatively activated by means of an electron-withdrawing α substituent. Anionic reagents other than carbanions have found application; these include anions of oxygen, nitrogen, selenium, and tin.

4.2.1.2.1. Organomagnesium Reagents

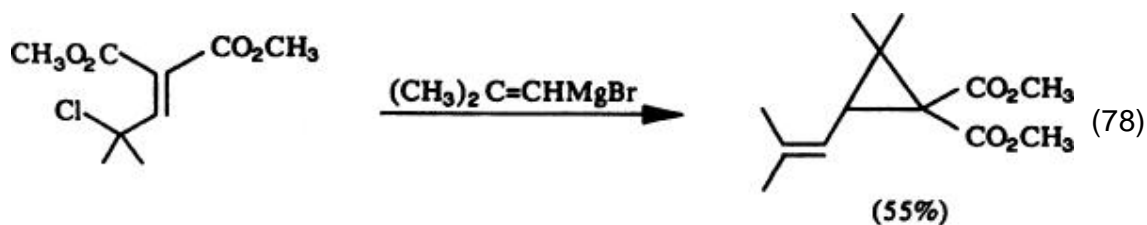
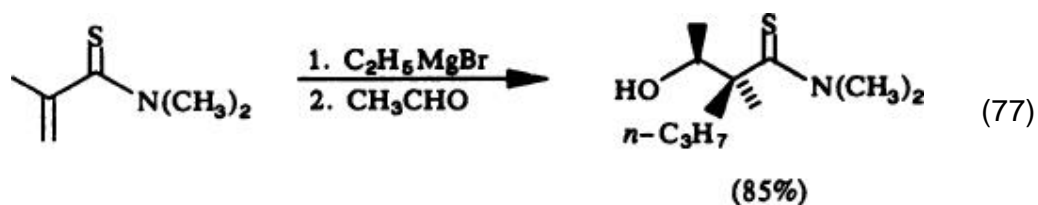
The historic significance of Grignard reagents in the development of the tandem vicinal difunctionalization of α , β -unsaturated carbonyl compounds has been mentioned. Rarely, Grignard reagents may initiate useful MIMIRC-type dimerizations of enones (Eq. 75), (19)

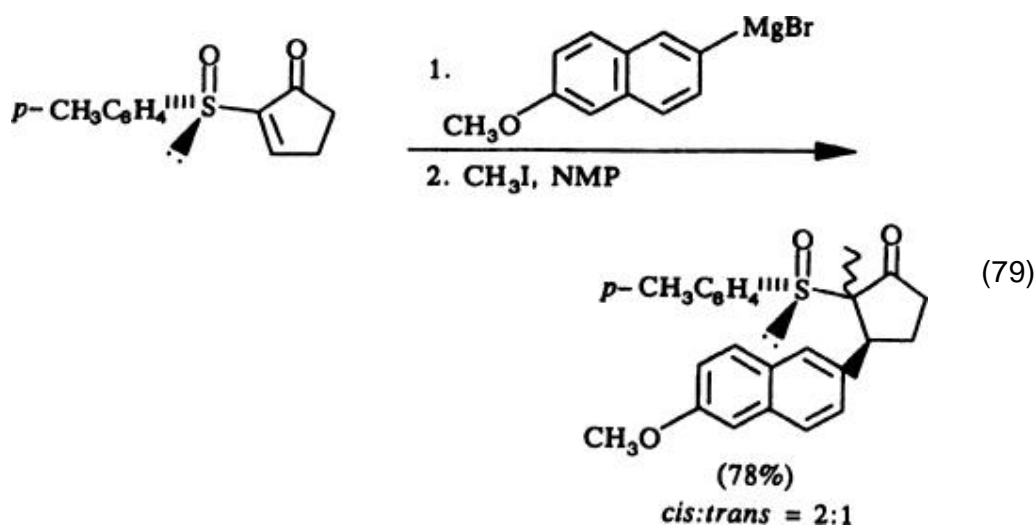


or can act as Michael donors to give dialkylation products (78) with unactivated enones. Typically, Michael acceptors that demonstrate affinity for 1,4 additions with unstabilized reagents are chosen in order to obtain good chemical yields of the desired products. Such acceptors include amides (Eq. 76), (190)



thioamides (Eq. 77), (191) and esters or ketones with α -alkoxycarbonyl (80) (Eq. 78) or arylsulfinyl (192) substituents (Eq. 79; 1-methyl-2-pyrrolidinone, NMP).

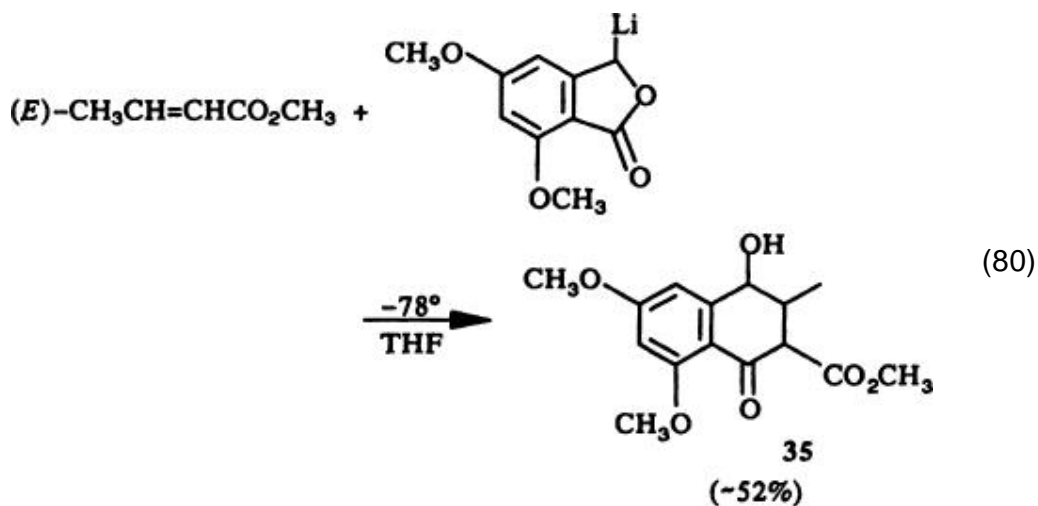




There appears to be little restriction on the identity of the organomagnesium reagent itself; primary, secondary, vinylic, and arylmagnesium halides can all be used without complication.

4.2.1.2.2. Organolithium Reagents

These relatively basic nucleophiles initiate tandem difunctionalizations via conjugate additions to α , β -unsaturated amides (190, 193) and thioamides (194) much like their organomagnesium analogs. Elaborated benzyl lithium reagents can react with esters, as evidenced by the preparation of tetralone **35** from methyl crotonate (Eq. 80). (195) Other alkyllithium

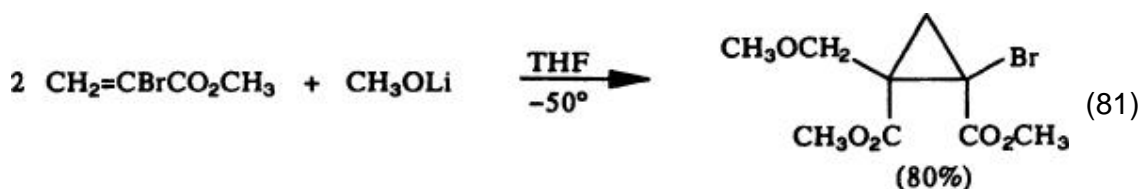


reagents usually will attack at the carbonyl moiety, resulting in 1,2 addition unless steric interactions between substrate and nucleophile retard or prevent this mode of attack. In such cases, efficient sterically directed β -addition- α -alkylation is observed. (196) Appropriately α' -substituted α , β -unsaturated

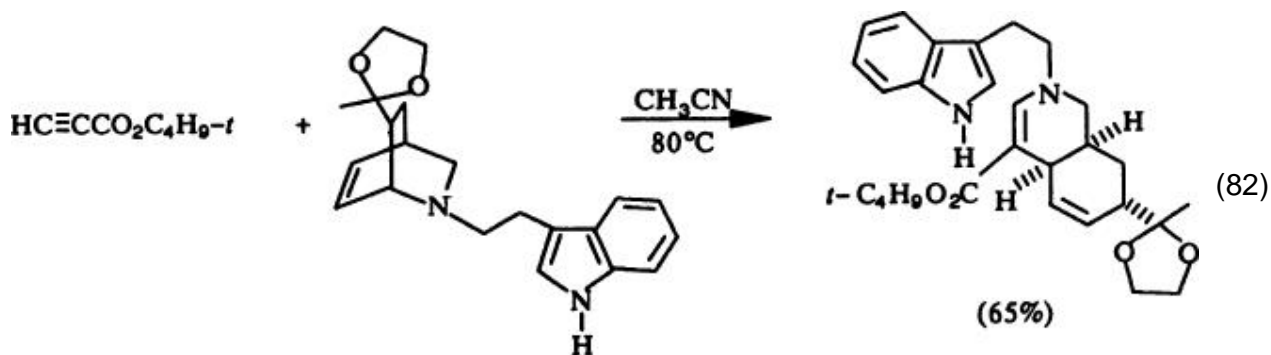
ketones follow a similar reaction pathway initiated by charge-directed conjugate addition of an organolithium reagent. (197-201)

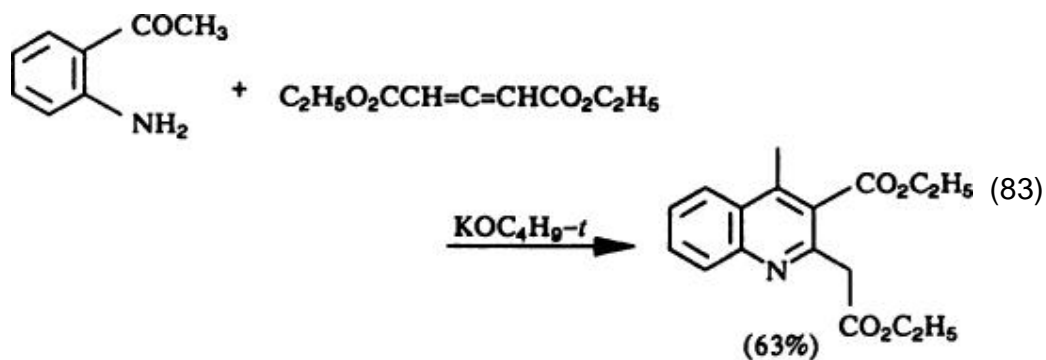
4.2.1.2.3. Alcohol and Amine Reagents

The use of alkoxide reagents in tandem difunctionalization reactions has been limited. The oxygen analogs of organosulfur Michael donors are used in preparations of β -butyrolactones (148) via the MIRC process (see Eq. 60) and in a similar reaction sequence for the synthesis of a chromone (Eq. 61). (149) Lithium alkoxide-initiated MIMIRC dimerizations of α -bromoacrylates result in stereospecific syntheses of tetrasubstituted cyclopropanes (Eq. 81). (141)

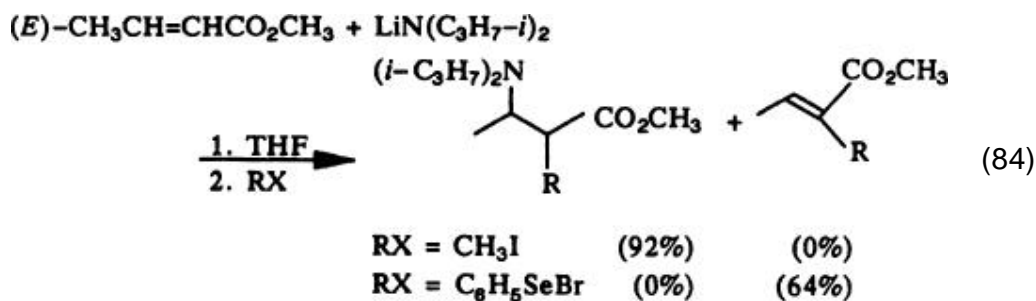


Amine reagents are of greater utility, particularly in syntheses directed toward heterocycles and complex alkaloids. Yohimbanes can be prepared via an amino-Claisen rearrangement strategy (Eq. 82); (202) preparations of quinoline nuclei are also possible (Eq. 83). (149) Direct comparison of amines with



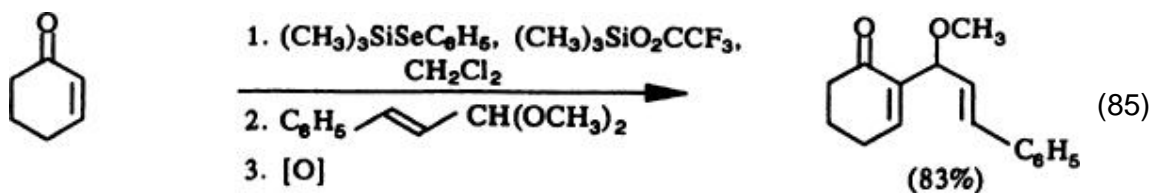


mercaptides as Michael donors in tandem difunctionalizations shows that yields may be lower with the former. (147) In certain cases, hindered amide bases such as lithium diisopropylamide (LDA) can act in similar fashion. (190, 203) Conjugate addition of lithium diisopropylamide to methyl crotonate proceeds efficiently, and the resultant conjugate enolate is captured easily with methyl iodide. When phenylselenenyl bromide is used as the α -functionalizing reagent, a *syn* elimination of the β -diisopropylamino group occurs in situ; and the α -phenylselenenyl ester is isolated as the only product (Eq. 84). (203)



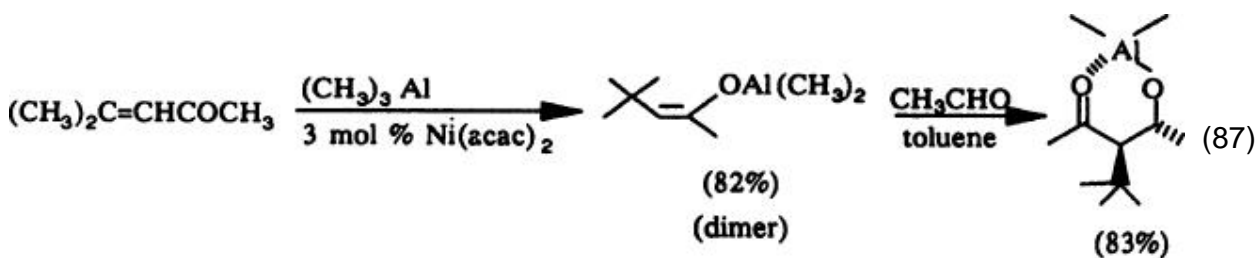
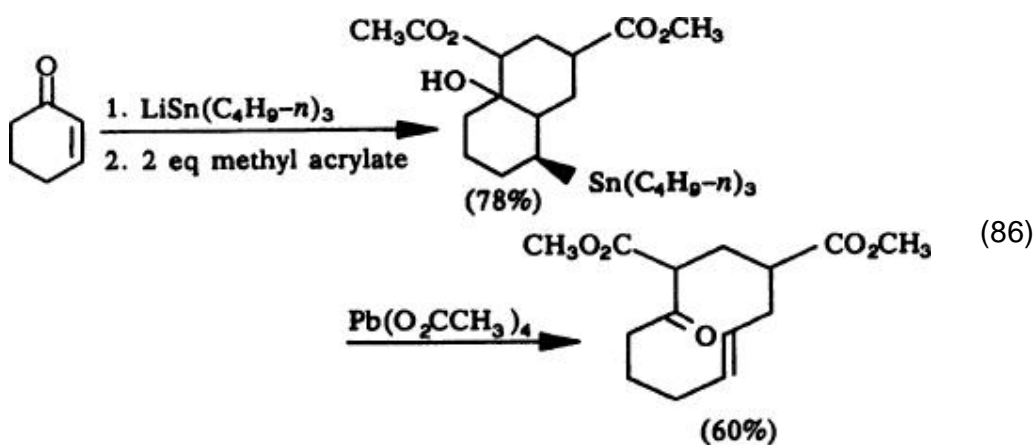
4.2.1.2.4. Other Reagents

Alkylselenodimethylaluminum reagents act as Michael donors of alkylselenide synthons when reacted with α , β -unsaturated ketones and are analogous to alkylthiodimethylaluminum reagents. (204) Alternatively, trimethylsilyl triflate-mediated cleavage of phenyltrimethylsilylselenide generates a selenonucleophile. The phenylselenide generates a β -phenylseleno conjugate enolate which is α -functionalized and subsequently undergoes oxidative *syn* elimination of phenylselenenic acid to give α -functionalized α , β -unsaturated ketones (Eq. 85). (205)

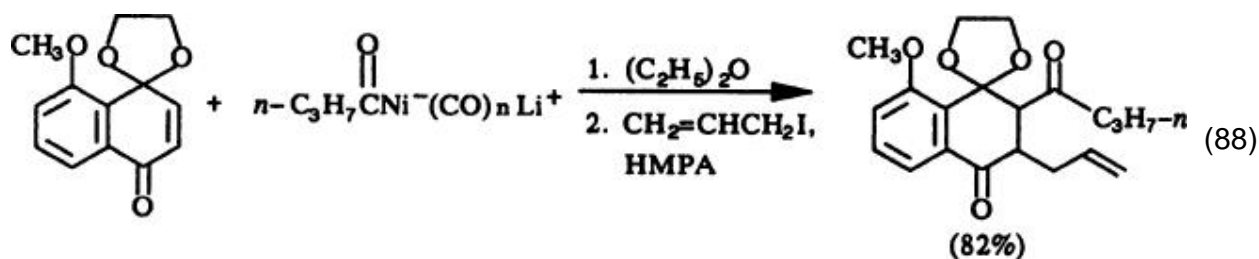


Trialkylstannyllithium reagents initiate tandem vicinal difunctionalizations of α , β -unsaturated ketones, resulting in β -stannyl ketones. (206) Used in a three-component, four carbon-carbon bond forming MIMIRC-type sequence, the product stannane undergoes oxidative ring enlargement to produce cyclodecenones (Eq. 86). (168)

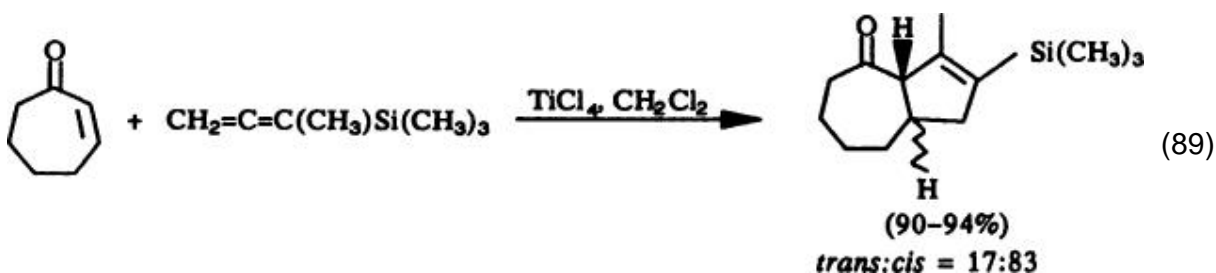
Organoaluminum and organozirconium reagents react with enones using nickel(II) catalysis; (207-209) such tandem difunctionalizations lead to prostaglandin intermediates (210) and new organoaluminum species (Eq. 87). (208) In a rare example of β -hydride addition followed by α -alkylation, diisobutylaluminum hydride-hexamethylphosphoric triamide functions effectively. (211) Acylate-nickel 1,4 additions to quinone monoketals followed by trapping of the conjugate



enolate with carbon electrophiles provide pivotal intermediates for the synthesis of isochromanone antibiotics (Eq. 88). (212)



Finally, attention should be brought to tandem vicinal annulation reactions of organosilane reagents using titanium (IV) chloride (213, 214) and tetrakis(triphenylphosphine)palladium. (215) Unsaturated ketones and esters are used as substrates and excellent stereocontrol typically is observed (Eq. 89). (214)



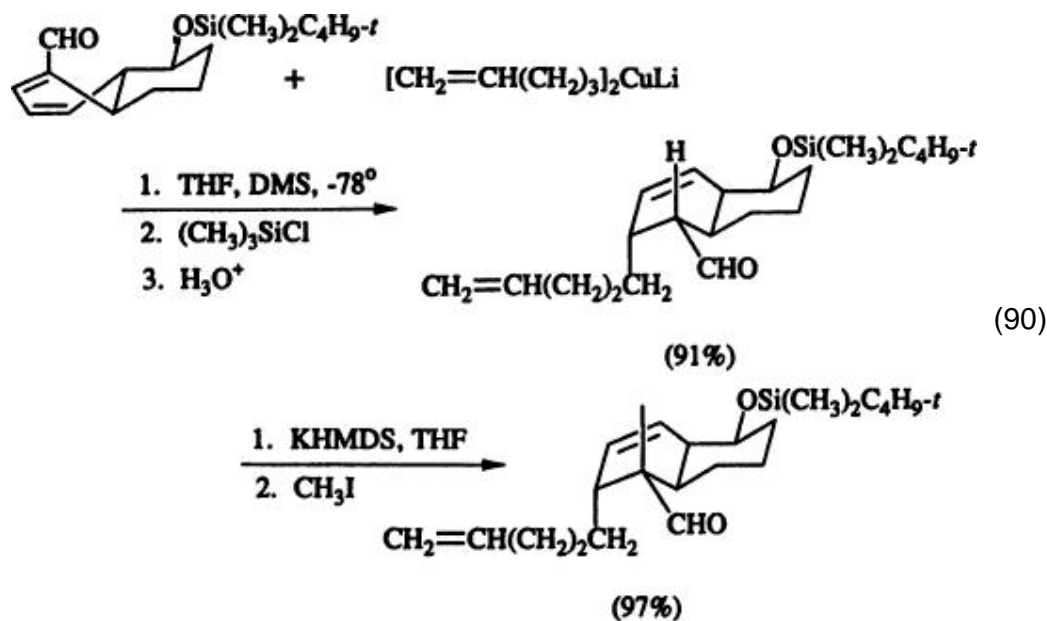
4.3. The α , β -Unsaturated Carbonyl Substrate

The broad variety of α , β -unsaturated ketones and esters that can be used in tandem vicinal difunctionalization sequences allows several factors and trends to be discussed. Other substrates such as aldehydes and amides have received less attention, making reactivity predictions more difficult and less reliable. Additionally, a family of noncarbonyl Michael-type acceptors such as vinylic nitriles, isoxazolines, and sulfones are good substrates for the tandem difunctionalization reaction.

4.3.1.1. Acyclic Enals and Enones

Conjugate addition–enolate trapping reactions of α , β -unsaturated aldehydes have not been widely explored. Cyclopropanations are possible using bromomalonates. (216) The aldehyde substrates appear to behave in a manner similar to analogous ketones in organocopper 1,4 addition–conjugate enolate alkylation, (102) with both comparable yields and high

diastereoselectivity resulting from net *trans* difunctionalization. A recent synthesis of a degradation product of the antitumor antibiotic chlorothricin illustrates this observation by achieving net *trans* dialkylation of an α, γ -dialdehyde with complete regio- and stereocontrol (Eq. 90; potassium hexamethyldisilazide, KHMDS); (217) no 1,6 addition was expected or observed



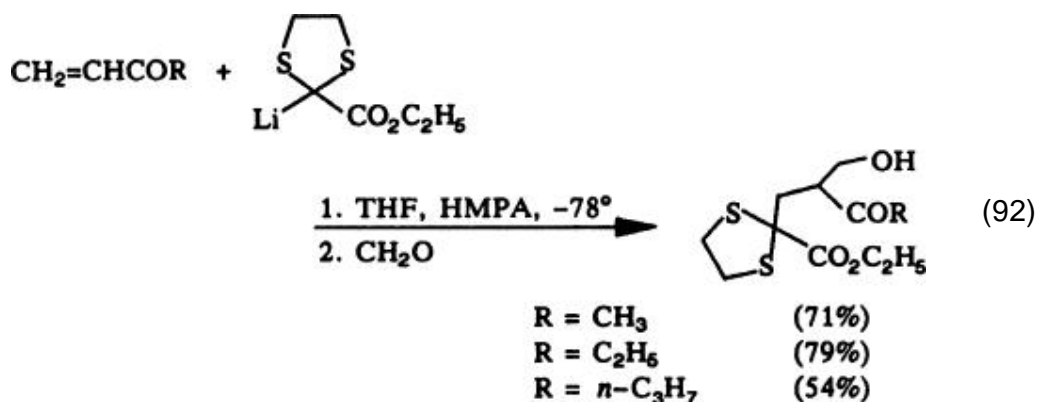
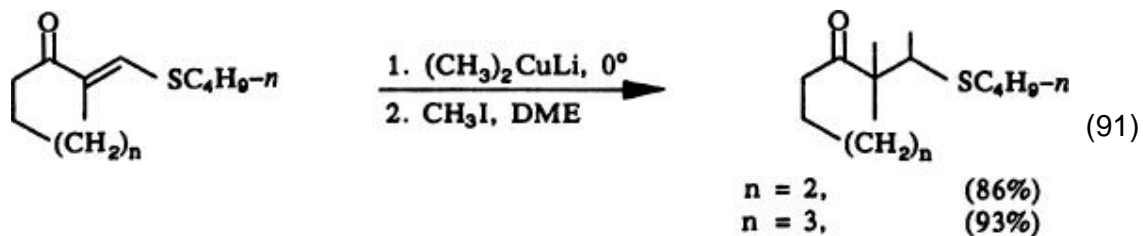
owing to the twisted orientation of the diene moiety of the substrate. Michael additions of enolates to α, β -unsaturated aldehydes as the initiating step in a MIMIRC reaction proceed well. (218) Isolated yields, however, tend to be lower than those from the corresponding ketones.

In contrast to acyclic enals, acyclic enones have been studied in detail. As in most reactions involving a 1,4 addition, the degree of substitution of the substrate has considerable influence on the success of the reaction. (219) Substituents at the α' carbon of the ketone appear to act as steric directors, shielding the carbonyl carbon from 1,2 attack and thereby enhancing 1,4 addition, but the degree of influence of the α' substituent varies depending upon the nature of the Michael donor.

For organocopper Michael donors, phenyl and benzyl vinyl ketones are superior substrates to methyl vinyl ketones. (102, 220) Exocyclic vinyl ketones are sensitive to ring size, a seven-membered ring being superior to a six-membered ring (Eq. 91; 1,2-dimethoxyethane, DME). (221)

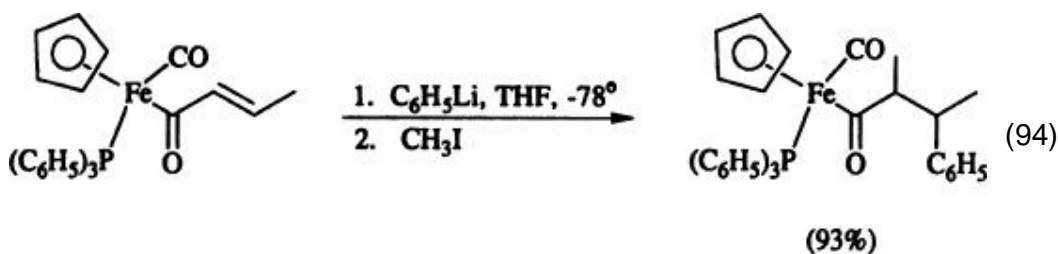
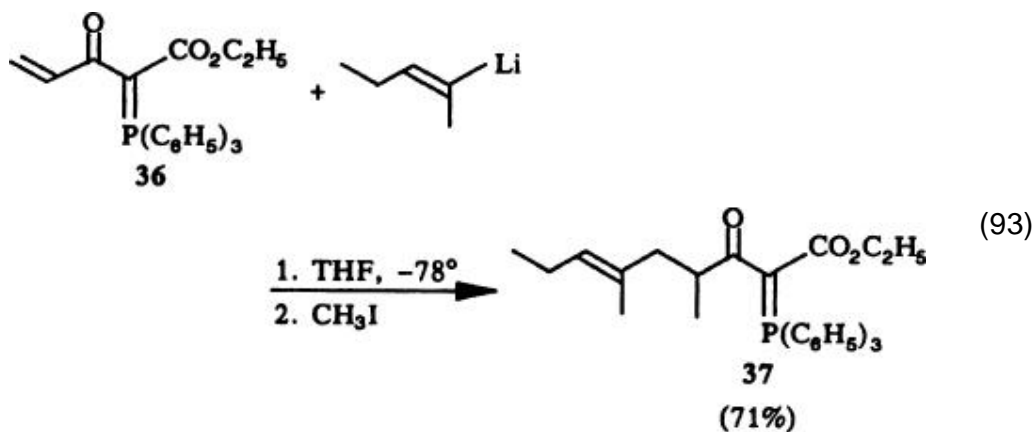
When enolates and acyl anion equivalents are used as Michael donors, methyl vinyl ketones are the poorest substrates and ethyl vinyl ketones the best, with

other groups falling in between (Eq. 92). (143, 222) The mesityl moiety of benzalacetomesitylene so hinders the carbonyl of the molecule that Wittig

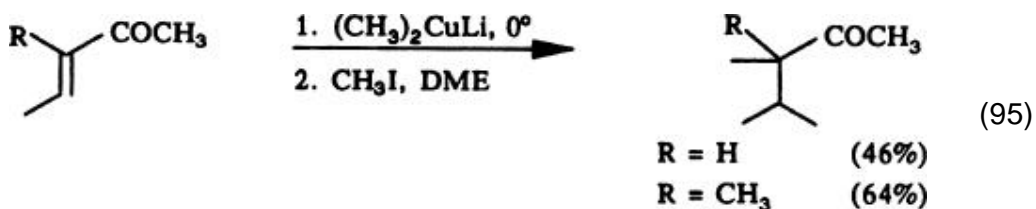


olefination using methylenetriphenylphosphorane is completely inhibited and instead a MIRC-type cyclopropanation is observed. (172)

A combination of large steric requirements and charge at the α' position of the substrate ketone results in charge-directed conjugate addition–enolate functionalization reactions. (197) Alkyl lithium reagents serve as Michael donors and the intermediate conjugate enolates are alkylated easily. (199) The (ethoxycarbonylmethylene)triphenylphosphorane **36** thus is elaborated into an acyl ylide **37**, which can be converted into a substituted ketone by subsequent decarboxylation and hydrolysis (Eq. 93). (198) Conceptually related to this approach is the use of α, β -unsaturated iron acyls as substrates for tandem vicinal dialkylations, (200, 223-225) which both activate the α, β -unsaturated acyl moiety toward 1,4 addition and provide excellent diastereofacial selectivity during the reaction sequence resulting in usually rare net *cis* dialkylation (Eq. 94). (200)

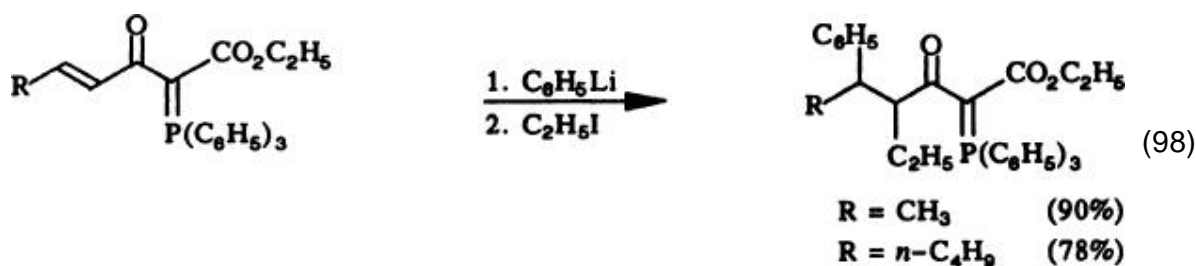
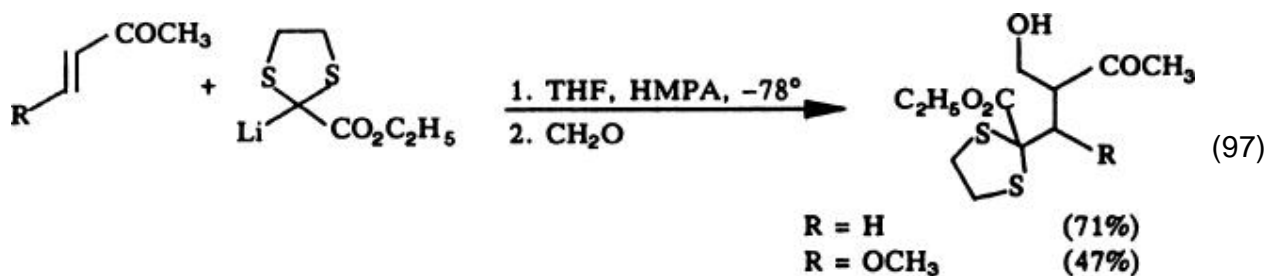
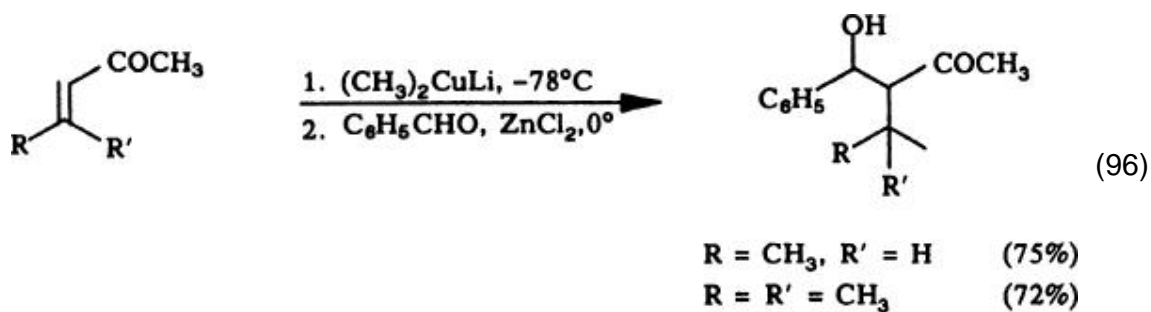


Substitution at the α carbon of the α, β -unsaturated ketone typically enhances the chemical yield of tandem difunctionalization reactions by retarding equilibration of the conjugate enolate intermediate before α -functionalization occurs. Invariably, when the α substituent is a methyl group, such enhancement is seen (Eq. 95), (221) but other, larger substituents may not provide similar results (*vide infra*).



Inasmuch as conjugate additions to enones display considerable steric sensitivity, increased substitution at the β carbon of an α, β -unsaturated ketone should be expected to decrease the overall reactivity of a Michael acceptor molecule. In the absence of Lewis acids, (219) β, β -disubstituted

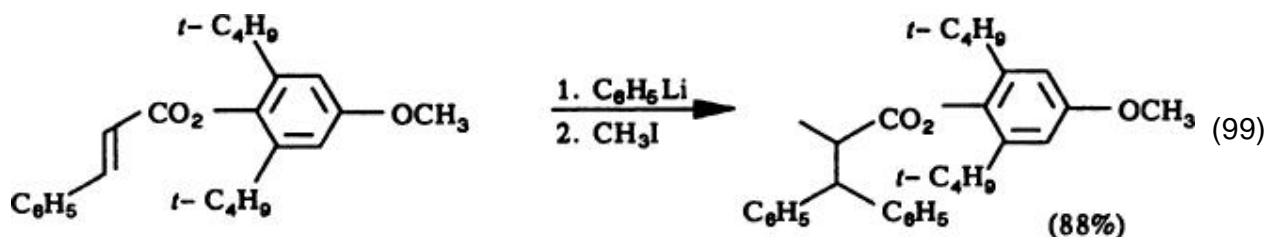
enones tend to be relatively poor substrates for tandem difunctionalization reactions involving bulky, highly stabilized Michael donors. Other reagents, most notably organocoppers and enolates, are not so discriminating with acyclic enone substrates; usually, only modest differences in reactivity or chemical yields are observed. For instance, conjugate addition–aldol condensation reactions of (*E*)-3-penten-2-one and dimedone indicate the minimal inhibiting effect of additional substitution at the β carbon of the substrate (Eq. 96). (220) More pronounced perturbations occur when steric and electronic factors (that deactivate the substrate as a Michael acceptor) are combined (Eq. 97). (222) The relative bulkiness of a β substituent may also influence the reactivity of the substrate in charge-directed vicinal dialkylation reactions (Eq. 98). (197, 198) Clearly, with differing reactants and reaction conditions it is not possible to predict a priori which β substituent may be more detrimental than another. (102)



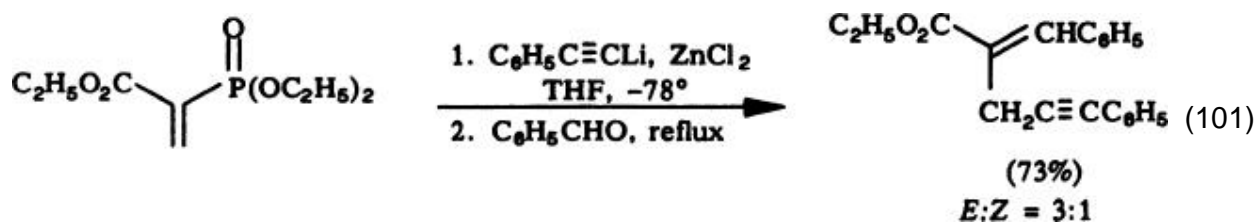
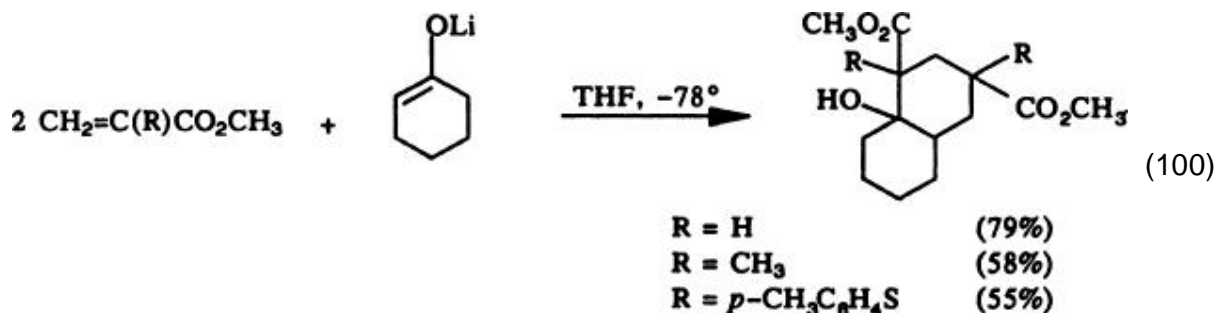
4.3.1.2. Acyclic Enoates and Enamides

Vicinal difunctionalization of α , β -unsaturated esters has been exploited widely. Acrylate polymers are valuable not only as commodity polymers, but also in the study of chain structures and conformation of molecules; enoates serve as the substrates of choice in many MIRC and MIMIRC reactions.

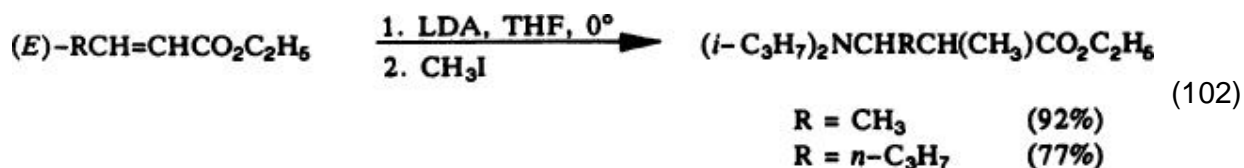
For most conjugate addition–alkylation reactions of alkyl alkenoates, the identity of the alkyl group is not critical in influencing the reaction sequence, although differences may be observable. (141) When a Michael donor is chosen that attacks the substrate not only in the desired 1,4 sense but also competitively in a 1,2 fashion, the choice of a very bulky alkyl moiety for the ester can bias the reaction toward 1,4 addition by steric inhibition of 1,2 addition (Eq. 99). (196)



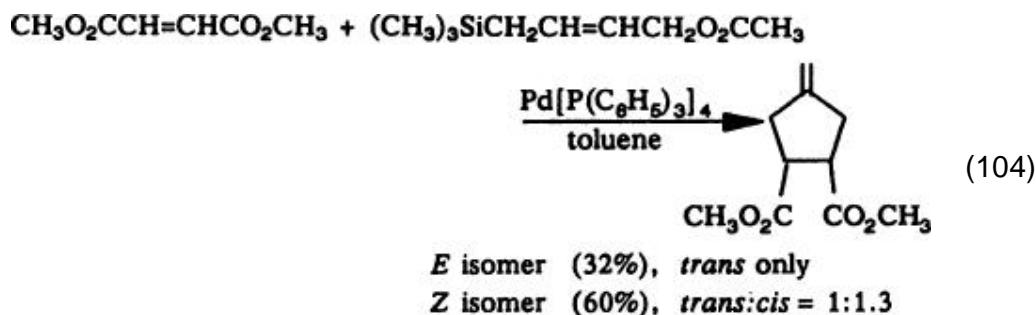
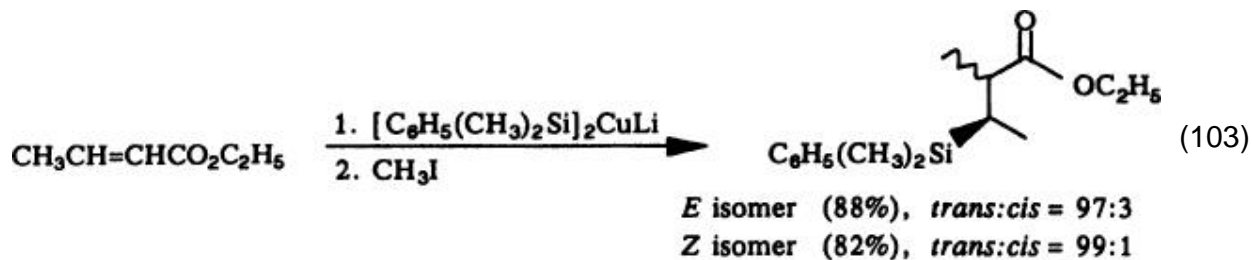
Substitution at the α carbon of an α , β -unsaturated ester in simple difunctionalization sequences again does not alter the course of the sequence significantly. Conjugate addition of phenylthiomagnesium iodide to either methyl acrylate or methyl methacrylate followed by aldol condensation gives essentially identical yields of the β -hydroxy esters. (145) In sterically demanding MIMIRC-type reactions, α -substitution reduces chemical yields of the products, but the specific size or nature of the substituent itself appears to be of less importance (Eq. 100). (226) A simple strategy to activate enoates toward tandem vicinal difunctionalization is to employ an α electron-withdrawing substituent such as a diethoxyphosphinyl group (Eq. 101), (165) an alkoxy carbonyl group, (80, 215, 227) or a cyano group. (177) The additional electron-withdrawing group usually imparts sufficient reactivity to permit alkyllithium and Grignard reagents to act as Michael donors.



Enoates substituted at the β carbon experience increasing sluggishness in the conjugate addition step of the difunctionalization sequence as the steric bulk of the substituent(s) increases. Influence on chemical yields can be significant (Eq. 102), (203, 215) although this may not always be the case. (145, 173) One interesting example indicates that (*E*)-crotonates are preferred to (*Z*)-crotonates



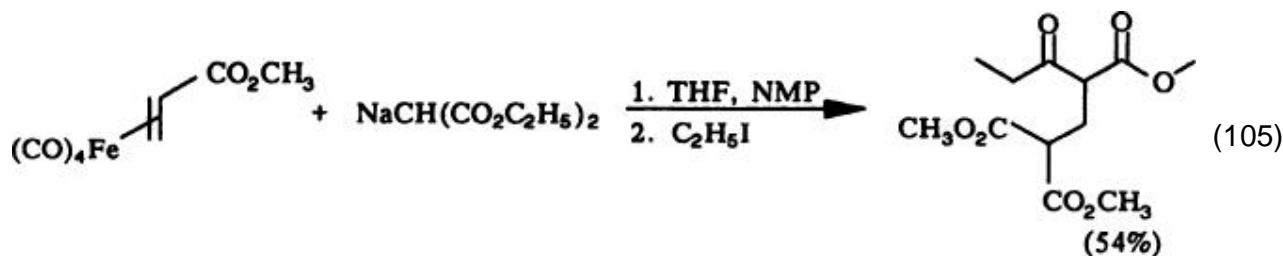
as substrates in organocopper 1,4 addition–conjugate enolate alkylations (Eq. 103). (102) In a similar case, palladium-catalyzed MIRC-type reactions of maleates proceed with greater facility than those of fumarates. Diastereoselectivity of the reaction is less, however, when the former substrate is employed (Eq. 104). (215) Methyl α , β -di(methoxycarbonyl)acrylate undergoes

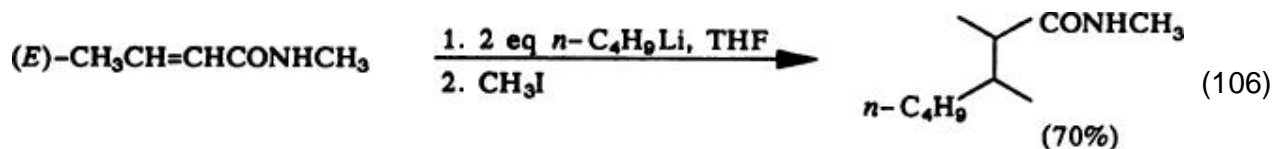


high-yield indirect MIRC-type cyclopropanation using 2-nitro-2-propylmetal reagents as Michael donors followed by protonation and sodium hydride-mediated ring closure via an $\text{S}_{\text{N}}1$ process. (178)

Tandem vicinal dialkylations of α , β -unsaturated esters may be mediated by their corresponding tetracarbonyliron complexes. (228) Crotonates are less reactive than acrylates; the conjugate iron enolates undergo carbonyl insertion into the carbon–iron enolate bond and subsequent alkylation affords β -ketoesters (Eq. 105).

Secondary and tertiary α , β -unsaturated amides and tertiary thioamides undergo 1,4 addition–conjugate enolate alkylation reactions using alkyllithium or Grignard reagents as Michael donors. (190, 191, 194, 229) Two equivalents of the alkylmetal reagent must be used for secondary amide substrates, the first to deprotonate the amide and the second to undergo conjugate addition (Eq. 106). (190) Alternatively, a secondary amide can be protected as an *N*-alkyl-*N*-trimethylsilylamide (191)





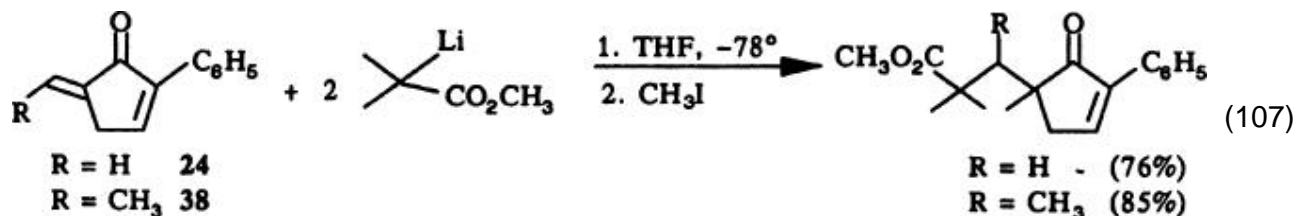
before submission to tandem vicinal dialkylation.

N-Alkyl-*N,N*-dialkylamino enamides, which are particularly inert to 1,2-addition reactions, also serve as substrates for the reaction sequence.

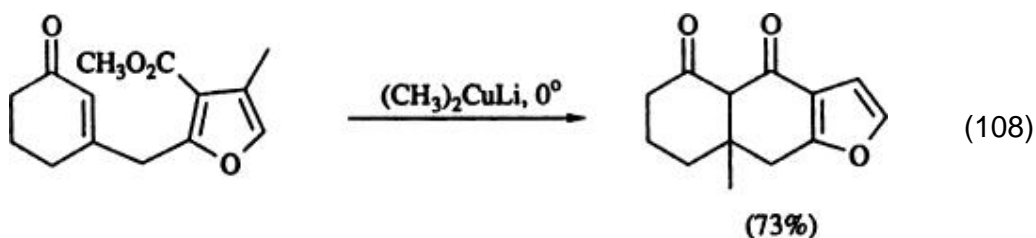
(193)

4.3.1.3. Cyclic Enones and Enoates

Owing to the wide occurrence of α , β -disubstituted cycloalkanones in nature, many tandem difunctionalization reactions of 2-cycloalkanones of moderate (5–8) ring size have been performed. General trends, especially for cyclopentenones and cyclohexenones, can be seen and employed in the design of efficient substrates for the reaction sequence. The influence of ring size on the rate of equilibration of the intermediate conjugate enolate is of primary concern. Cyclopentanone enolates equilibrate rapidly with respect to cyclohexanone enolates (118) so that regioselectivity of α -alkylation of such conjugate enolates can be lost if the reaction conditions are not chosen with care. Consequently, α substituents capable of stabilizing the conjugate enolate are employed to circumvent this problem. 2-Methyl-2-cyclopentenone appears to be a superior substrate for tandem vicinal difunctionalization when compared to 2-cyclopentenone, but larger alkyl substituents can reduce the effectiveness of the reaction sequence; 2-ethyl-2-cyclopentenone, for instance, is an inferior substrate to the 2-methyl analog. (114) Arylhetero substituents, on the other hand, both stabilize the conjugate enolate of the substrate toward equilibration and enhance α -alkylation. Ketones such as 2-phenylthio (90, 125) and 2-phenylselenyl-2-cyclopentenone (230) are 2-cyclopentenone synthetic equivalents which offer better stereo- and regiocontrol of the difunctionalization sequence. Enantiomerically pure 2-arylsulfinyl-2-cycloalkanones function similarly, with the additional ability to provide directable diastereofacial bias during conjugate addition, (231) producing 2,3-disubstituted cycloalkanones with high enantiomeric purities (e.g., Eq. 79). (192) Substitution at the β carbon of the cycloalkanone retards the rate of conjugate addition and can lower the degree of stereo- and regiocontrol as well as the chemical yield of the reaction. (232) Cycloalkanones are intrinsically less reactive than β -unsubstituted enones. A synthetically useful exploitation of this observation employs substrate 24, which undergoes regioselective tandem difunctionalization at the exocyclic double bond; the exocyclic enone still is attacked exclusively even if β -substituted as in substrate 38 (135) (Eq. 107).

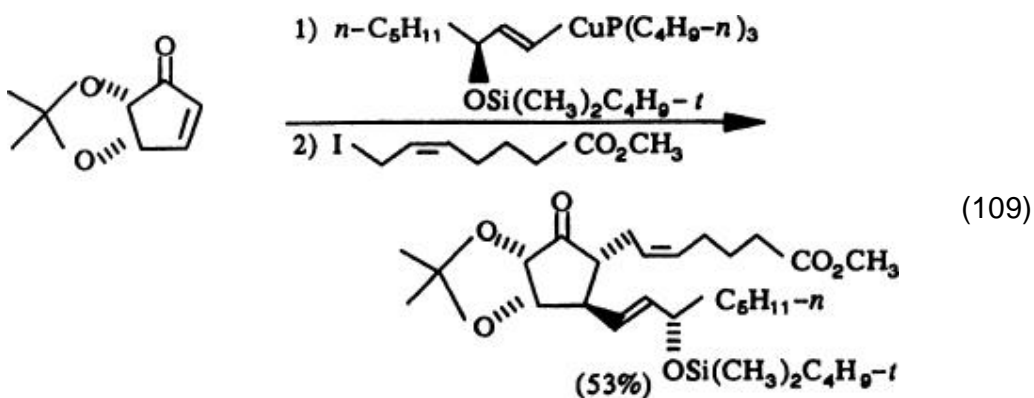


Stereospecific formation of norbornanones is possible when a MIMIRC synthetic strategy is used (Scheme 8). (136) In a similar vein, β -substituted cycloalkenones may be more reactive than β, β -disubstituted esters (Eq. 108). (233)

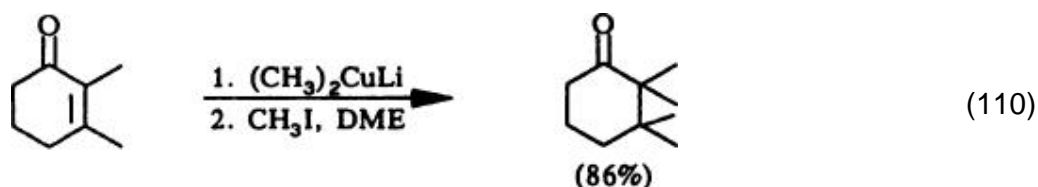


Lewis-acid catalysis of the conjugate addition can greatly enhance the rate at which β -substituted cycloalkenones react. (219)

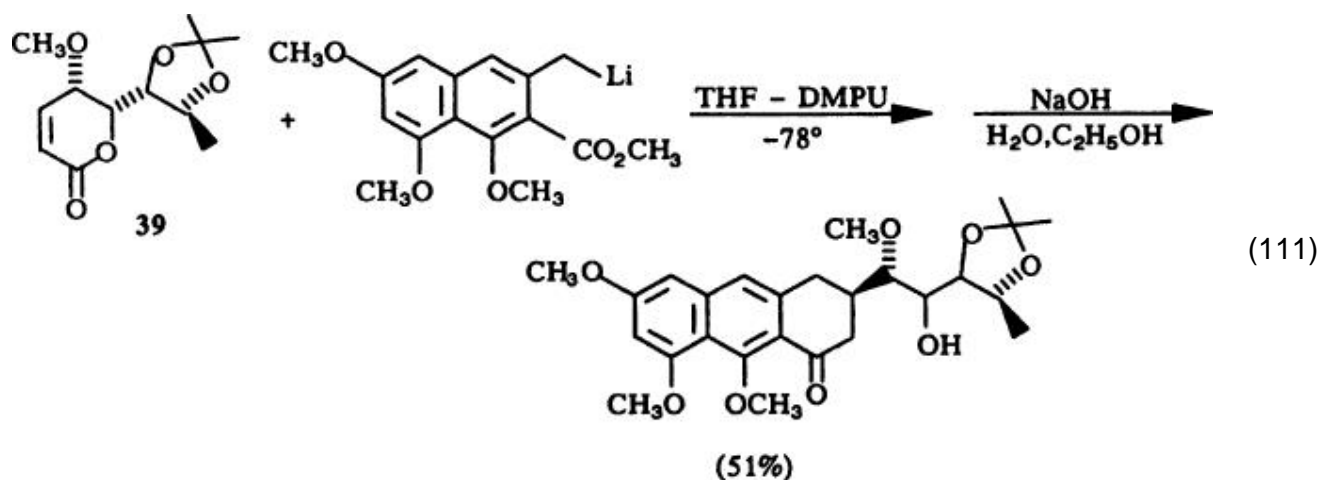
Alkyl substituents at carbons of the cycloalkenone other than those of the alkenyl moiety typically do not interfere with the reaction sequence, (234) for example, 4,4-dimethyl-2-cyclopentenone (235) and 5,5-dimethyl-2-cyclopentenone, (236) and function similarly as substrates in the tandem vicinal dialkylation reaction sequence (in the latter case the question of conjugate enolate equilibration is moot). Strategically placed substituents on cyclopentenones are used as combined diastereofacial-biasing and conjugate enolate equilibration-inhibiting elements in total syntheses of prostaglandins (Eq. 109). (74, 237)



A combination of α - and β -substitution provides substrate molecules for the construction of vicinal quaternary carbon centers. (238) Although enolate equilibration (232) and steric congestion (239, 240) can prevent the straightforward application of the methodology, adjacent quaternary center construction can be successful (Eq. 110). (221, 241)



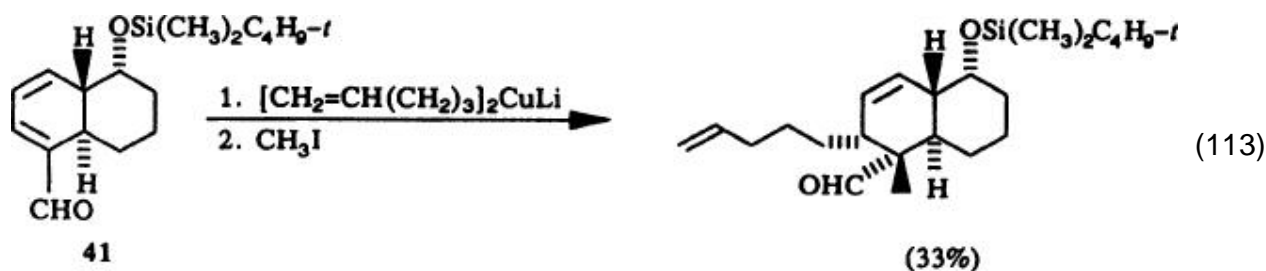
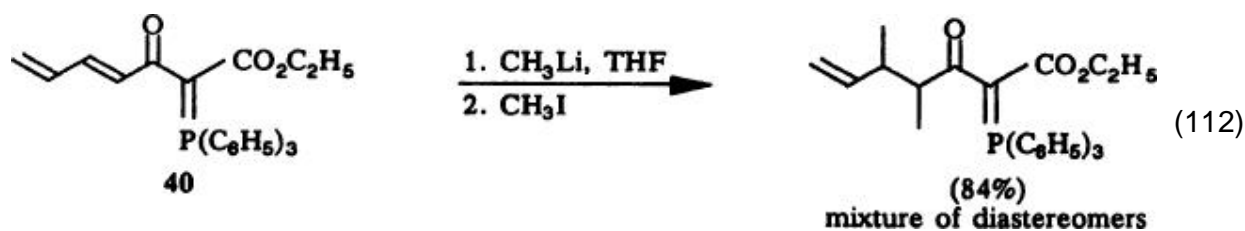
Cyclic enoates, or alkenolides, have not often been employed as substrates for tandem vicinal difunctionalization reactions. Those enjoying the greatest use are γ -butenolides and 4-substituted γ -butenolides, which are used in the total syntheses of lignans (159, 162, 163) and prostaglandin analogs (Eqs. 32, 67). (103) The reaction sequence is well behaved and yields of the products usually are quite high. δ -Pentenolide **39** undergoes a stereospecific Michael–Claisen difunctionalization sequence, resulting in an anthracenone used for the synthesis of olivomycin A (195) (Eq. 111, *N,N* -dimethyl-*N,N* -propyleneurea, DMPU).



4.3.1.4. Polyunsaturated Ketones and Esters

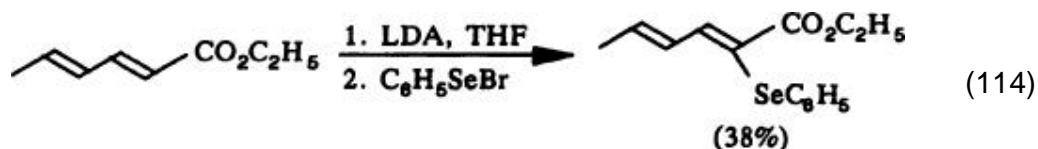
Multiply unsaturated ketones and esters can undergo “extended” Michael additions. For instance, 2,4-dienones may undergo 1,6 conjugate addition (242)

as well as 1,4 conjugate addition with a Michael donor; for 2,4,6-trienones, 1,8, 1,6, and 1,4 addition modes all are possible. (243) Application of tandem vicinal dialkylation methodologies to these substrates has received limited attention. Dienone **40** undergoes exclusive 1,4 addition of methyl lithium, with subsequent C-methylation of the conjugate enolate proceeding in good yield (Eq. 112). (197) Similarly, dienal **41** functions as a substrate for exclusive 1,4 addition (Eq. 113; cf. Eq. 90). (217) Other related additions include organocoppers to fulvenes, (244) alkylolithiums to 2-naphthyloxazolines, (245, 246) and arene–chromium tricarbonyl complexes; (247) in each case,



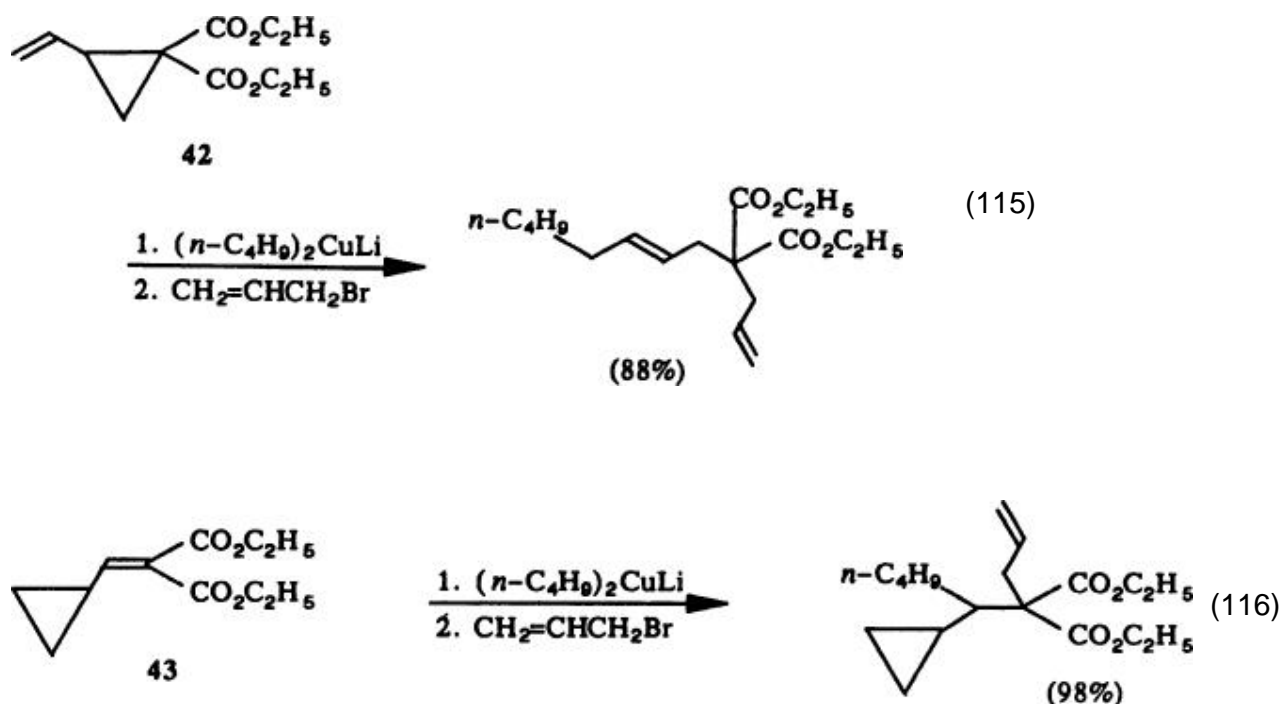
only 1,4 addition is observed. As might be expected, the same behavior is observed for α , β -unsaturated ketones and esters bearing β -aryl substituents. (19, 67, 172, 177, 220)

Transient vicinal difunctionalization is exploited to incorporate the α -phenylseleno moiety into α , β -unsaturated esters; (203) extension to polyunsaturated esters also results in the same regiochemistry (Eq. 114).



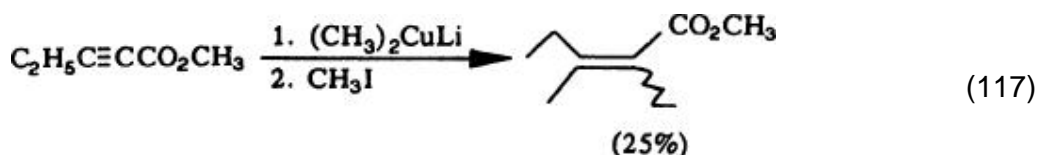
Cyclopropane **42** is a related substrate in which 1,6-type addition is obtained when an organocopper reagent is used as Michael donor. (227) The resultant

enolate C-alkylates to afford net 2,6-dialkylation of 4-hexenoates (Eq. 116). On the other hand, when cyclopropane **43** is reacted under identical conditions, the 2,3-dialkylation product results (Eq. 116).

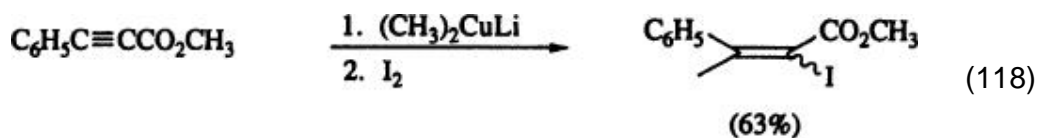


4.3.1.5. Acetylenic and Allenic Carbonyl Substrates

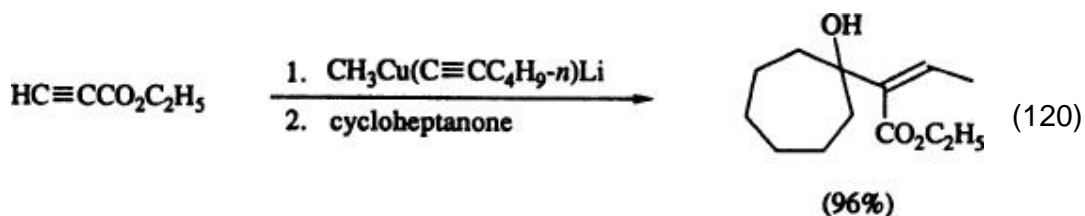
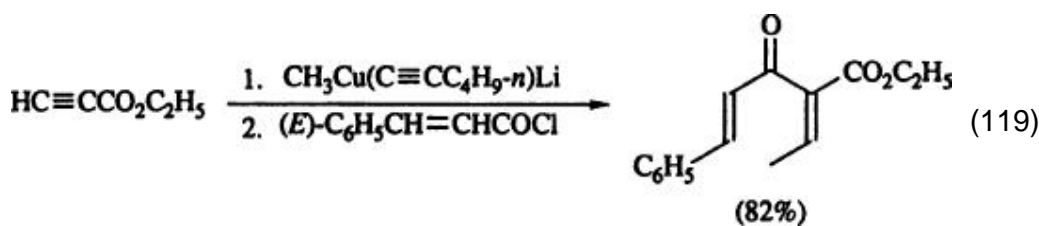
The use of acetylenic ketones and esters as substrates for tandem vicinal difunctionalization reactions sometimes provides a route to activated olefins of high isomeric purity. Much like the stereospecific *cis* addition of organocopper reagents to alkynes, (6, 248) 1,4 addition of an organocopper to an α -acetylenic ketone or ester begins with net *cis* addition to give a vinylic organocopper intermediate. The reactivity of the electrophile that is added to complete the reaction sequence determines if the intermediate is trapped prior to equilibration through an allenolate species (Scheme 9). (249) The product geometry ratio depends upon the steric interactions between allenolate and electrophile. Many examples indicate that loss of the stereo integrity of the intermediate vinylic organocopper species is common; such is the case for methylation (Eq. 117), (97) chlorination, (249) and iodination (Eq. 119). (96, 250) Bromination appears to be stereospecific



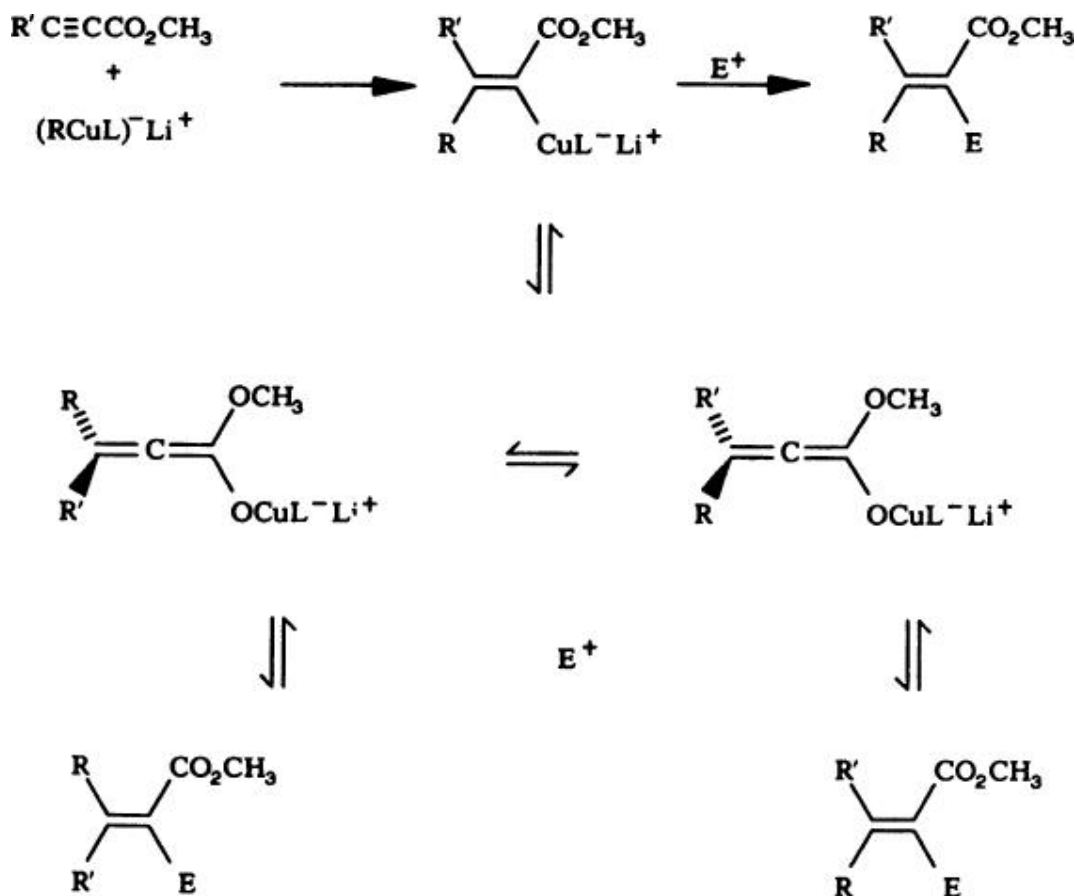
in the opposite sense to the other halogens, but also yields products from reductive dimerization of the resultant vinyl bromide. (249) The ratio of isomeric olefins produced can be controlled by changing the counterion of the intermediate allenolate. (250) Acid chlorides appear to be sufficiently reactive electrophiles to give only net *cis* dialkylation; bulky electrophiles result in net *trans* dialkylation (Eqs. 119 and 120). (110, 249) The allenolate intermediates of



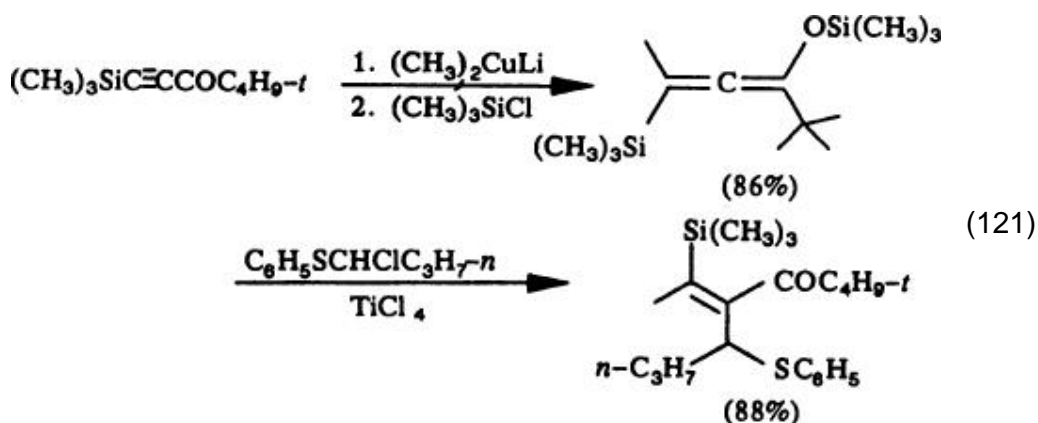
α -acetylenic ketones can be captured as allenol silyl ethers and subsequently α -alkylated (Eq. 121). (251)



Scheme 9.



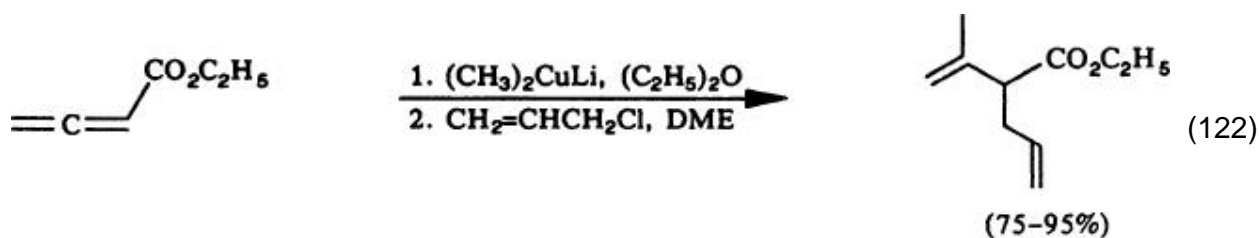
Allenates of α -acetylenic esters appear to be less prone to equilibration than those of corresponding α -acetylenic ketones. Propiolate esters undergo *trans*-vicinal distannylations using 2.5 equivalents of a stannylcopper reagent (Eq. 45). (94) The product alkenes subsequently can be regioselectively transmetalated at the α carbon and alkylated to give α -alkyl- β -stannyl- α, β -unsaturated esters. Complementary *cis* distannylation is obtained by palladium-catalyzed addition of hexamethyldistannane. (252) *N,N*-Dimethyl α -acetylenic amides, when reacted with one equivalent of trimethylstannylcopper, are



β -trimethylstannylated; the conjugate anion can be α -alkylated in useful yields. (95)

Acetylenic esters can function as substrates for MIRC-based synthetic strategies, providing preparations of highly substituted cycloalkenones (99) and α , β -unsaturated lactones. (253, 254) Hydroisoquinolines can be prepared via a conjugate-addition–amino-Claisen rearrangement sequence (Eq. 82); these products can be transformed into yohimbines. (202)

Allenic esters and ketones undergo 1,4 additions smoothly with organocopper reagents. The resultant conjugate enolates can be C-alkylated in dimethoxyethane, producing β , γ -unsaturated ketones and esters (Eq. 122). (255) The use of allene 1,3-diester as substrates for MIRC-based heterocycle synthesis yields pyrazines, pyrazoles, quinolines, and thiophenes (Eq. 61), as well as other heterocyclic systems. (149)



4.3.1.6. Functional Group Compatibility

Any functional group in the substrate that will not react with the Michael donor reagent or the conjugate enolate can be considered fully compatible. If a group's reaction rates with the initial Michael donor or the conjugate enolate are low compared with those reactions leading to the desired product, it will be tolerated. Most substituents with low nucleofugacity—alkoxy, alkylthio or alkylseleno groups, tertiary amino moieties, and ketals or acetals—rarely interfere. Electrophilic substituents, however, should be viewed with caution on two counts. Possible competition for the Michael donor reagent should be considered. Furthermore, when appropriately located in the substrate, such groups may compete with an extramolecular electrophile for alkylation of the conjugate enolate, resulting in MIRC-type products. Protected forms of carbonyl moieties, nitriles, and some alkenes are preferred when such behavior is to be avoided. Halogens usually can be tolerated, especially chloroalkyl groups, because of the relative inertness of these groups as enolate alkylating reagents. Organocopper Michael donors, however, in certain circumstances can reductively cleave halogens from a substrate to generate a new reactive anion. Relatively acidic groups such as hydroxy and

sulfhydryl often can be deprotonated with a nonnucleophilic base without interference in the subsequent dialkylation, or can be protected to ensure no interference. Alkylsulfinyl, alkylsulfonyl, and other groups that can be deprotonated to stabilized anions may serve as Michael donors, thus initiating undesirable polymerizations. Arylsulfinyl and arylsulfonyl groups, like some halo substituents, can be cleaved reductively from the substrate when an organocopper Michael donor is employed. The electrophilic nature and the anion- and dianion-stabilizing capability of the nitro group mandate its protection. (256)

4.3.1.7. Miscellaneous Substrates

The tandem vicinal dialkylation strategy can be used successfully for a number of substrates analogous to α , β -unsaturated carbonyl compounds. Although beyond the scope of this review, a sampling of these substrates and their difunctionalized products is presented in Table A.

Table A. Miscellaneous Substrates for Tandem Vicinal Difunctionalization

[View PDF](#)

4.4. The α -Functionalizing Reagent


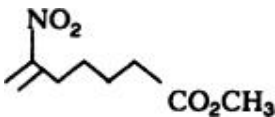
The choice of an α -functionalizing reagent for the conjugate enolate should be determined by the same factors that affect the C-alkylation of regioselectively generated enolates. Applicable generalizations follow. Any regioselectively generated enolate that *can* equilibrate *may* equilibrate. The enolate is an ambident anion that can demonstrate competitive O-alkylation versus C-alkylation. In the case of organocopper-derived conjugate enolates, C-alkylation can be sluggish and requires good electrophiles to succeed.

4.4.1.1. Nature of the Reagent

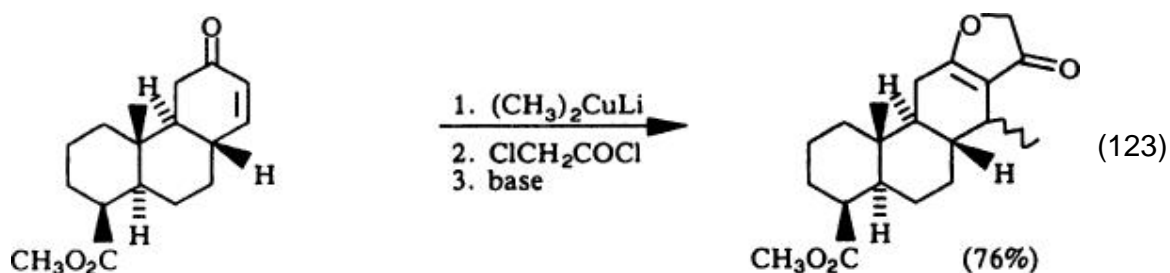
A wide variety of electrophilic α -functionalizing reagents can be employed in tandem vicinal difunctionalizations. The most common reagents are alkyl iodides, allyl and propargyl bromides, aldehydes, and ketones. Hard–soft Lewis acid–base theory has been used to explain why these reagents are relatively good α -alkylating agents. (267) Softer, more polarizable electrophilic reagents show not only enhanced reactivity, but also essentially complete C-regioselectivity under normal conditions. A review of the C-alkylation of regioselectively generated enolates discusses various electrophilic reagents.

(59) Table B lists some of the more popular α -functionalizing reagents used in α , β -difunctionalization reactions.

Table B. Some α -Functionalizing Reagents for Tandem Vicinal Difunctionalization

CH_3I	
$\text{CH}_2 = \text{CHCH}_2\text{Br}$	$\text{BrCH}_2\text{CO}_2\text{CH}_3$
$\text{CH}_2 = \text{C}(\text{COCH}_3) \text{Si}(\text{CH}_3)_3$	$\text{BrCH}_2\text{C} \equiv \text{CC}_2\text{H}_5$
H_2CO	$\text{C}_6\text{H}_5\text{SeBr}$
CH_3CHO	CO_2
$\text{C}_6\text{H}_5\text{CHO}$	$[(\text{CH}_3)_2\text{NCH}_2]^+\text{Cl}^-$
$(\text{C}_6\text{H}_5)_2\text{S}_2$	$[\text{CH}_2 = \text{CHP}(\text{C}_6\text{H}_5)_3]^+\text{Br}^-$
$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	$\text{CH}_2 = \text{CHCO}_2\text{CH}_3$
I_2	ethylene oxide
Br_2	acetone
$\text{HC}(\text{OC}_2\text{H}_5)_3$	cyclohexanone
	

Considerable research involving the use of acyl chlorides as α -functionalizing reagents indicates that *O*-acylation competes with *C*-acylation. (69) The ratio of products is dependent upon the nature of the reagent, (110, 268) the substrate, (269, 270) and the reaction conditions. (79, 271, 272) *O,C*-Diacylated products often are obtained, (273) but can be hydrolyzed to the desired α , β -difunctionalized product. The use of chloroacetyl chloride takes advantage of this observation, generating a butenolide fused to carbons 1 and 2 of the original substrate (Eq. 123); (274) crotonyl chloride gives similar results. (271)

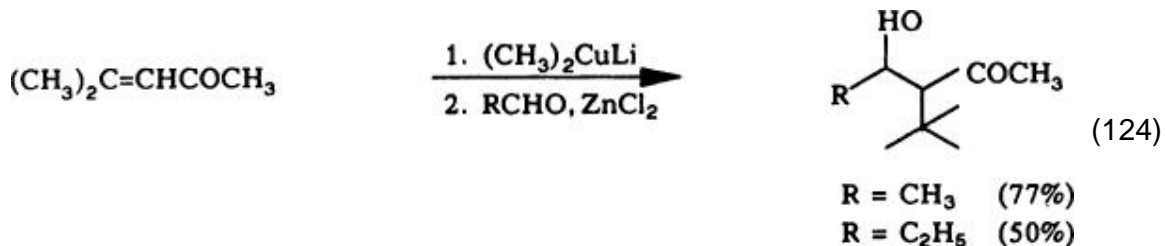


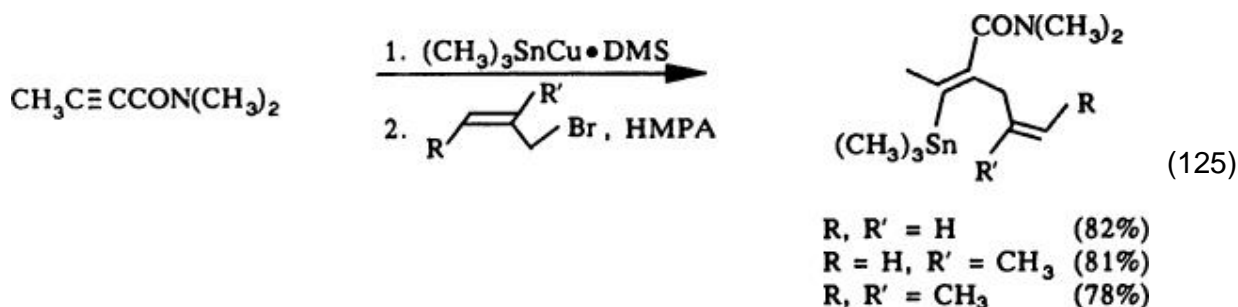
Reagents for α -functionalization may be intramolecular, giving ring closure in MIRC-based reactions. Such a reagent may be part of the original substrate (140, 213, 275, 276) or, more commonly, present in the Michael donor in either a masked (124, 202, 277, 278) or native state. (120, 227, 279) Yields in these cases generally are quite good owing to rate acceleration and decreased byproduct formation.

Bifunctional electrophilic reagents allow some generalization as to overall reactivity. Esters are quite unreactive, as are vinylic halides. Acyl halides, primary alkyl iodides, propargyl and allylic halides, α -halo esters, aldehydes, and nitroalkenes are among the most reactive reagents.

4.4.1.2. Effect of the Nature of the Reagent on the Yield of α -Functionalization

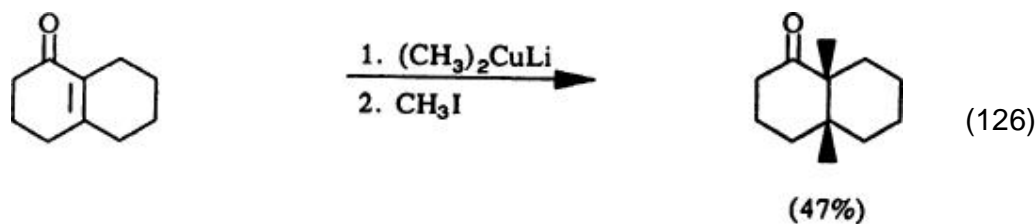
Only relatively reactive electrophiles result in good amounts of α -functionalization of the conjugate enolate. These electrophiles include methyl and primary alkyl iodides; propargylic, allylic, or benzylic halides; and aldehydes. Organocopper-derived conjugate enolates can be difficult to α -functionalize unless the following prescriptions are: use of the most reactive electrophiles and changes in solvent (221, 232, 280) or counterion. (220, 281) Within a series of homologous reagents, smaller electrophiles typically are more efficient than sterically larger ones (Eqs. 124 (220) and 125 (95)).





4.4.1.3. Effect of the Nature of the Reagent on the Stereochemistry of α -Functionalization

Thermodynamically more stable *trans* α , β -difunctionalized products are formed predominantly in the reaction sequences regardless of the electrophile. When the Michael donor is large, (114) small changes in the steric profile of the electrophile can result in complete stereoselectivity (Eq. 9). In the case of α , β -disubstituted enone substrates, steric approach control analysis is more predictive of the outcome than product development control; net *cis* dialkylation may result (Eq. 126). (232) Steric approach control may predominate



even when its operation requires formation of significantly less thermodynamically stable products (Eq. 79). (192)

4.4.1.4. Functional Group Compatibility

Relatively acidic functional groups such as hydroxy and sulfhydryl and those that facilitate deprotonation, such as β -ketoesters and alkylsulfinyl or alkylsulfonyl moieties, should not be present in the electrophile. Proton donors preclude α -functionalization by conjugate enolate quenching. Electrophilic reagents with several nucleofugal centers can be employed without problems if there is a significant difference in the electrophilicity of the moieties present in the reagent; a variety of these have found application in prostaglandin synthesis. (86, 258, 282-286) Various dihalides, (194, 261) α -halo esters, (100, 279) and α , β -unsaturated acid chlorides (110) also act as selective electrophilic α -functionalizing reagents.

5. Synthetic Utility

Tandem vicinal difunctionalization of an α , β -unsaturated carbonyl-containing substrate represents a convergent synthetic strategy that has considerable appeal and versatility. By linking a Michael-type addition and an enolate-mediated carbon-carbon bond-forming reaction through a variety of substrates, molecules with regiospecifically introduced multifunctional arrays are generated. Michael-aldol difunctionalizations of cycloalkenones provide 2-hydroxyalkyl-1,5-diones; 1,4-organocopper addition-alkylation difunctionalizations of propiolates produce stereoisomerically pure α , β -unsaturated esters. Cyclic 1,3-dicarbonyl functionality is obtained by Michael ring-closure reaction, for example, Michael addition followed by Dieckmann condensation. Sequential Michael ring-closure reactions yield complex polycyclic products that may be inaccessible through other routes. Conjugate addition-alkylations of allenyl ketones provide γ , δ -unsaturated ketones. Clearly, any of a number of permutations is possible, indicating the versatility of the technique.

The α , β -dialkylated carbonyl moiety is a common structural element in many natural products and a common synthetic element in organic chemistry. For these reasons, tandem vicinal difunctionalization has found considerable exploitation in natural product synthesis. Table C lists some of the natural products that have been prepared by the reaction sequence. It has been pivotal in the development of prostaglandin synthesis and is the method of choice for their preparation. (287) A variety of terpenoids have been prepared by the technique, (288) including steroids, (289, 290) many of whose syntheses have relied on tandem vicinal dialkylation to form the critical C-D ring juncture in a stereospecific manner. Polyketide-derived anthraquinones (195) can be prepared by the difunctionalization strategy. Modification of the Robinson annulation (291) has led to the preparation of *cis*- and *trans*-decalins, (292) hydrindanes, (293) and hydroazulenes. (294) The use of butenolides as substrates provides direct access to lactone antibiotics. (159, 295)

Table C. Some Natural Products Prepared Employing Tandem Vicinal Difunctionalization

Product	Reference
Aklavinone	153
Anthraquinones	195

Aromatin	164
Ascochlorin	301
Atisiranone	302
Avenaciolide	303
Bicyclo[3.2.1]octanes	123
Chlorothricolide	304
Clerodanes	292
Compactin	305
Coriamyrtin	306
Coriolin	307
Damascones	308
Eremolactone	295
Eriolanin	309
Galactin	158
Gascardic acid	310
Gymnomitrol	311
β -Himachalene	312
Hydrindanes	293
Hydroazulenes	247
Integerrimine	313
<i>trans</i> - γ -Irones	314
Ishwarone	315
Isostegane	162
Ivalin	262
Khusimone	127
Lanvandulol	255
Laurene	316
Longifolene	317
Lycopodine	26
Methyl jasmonate	318
Methyl vouacapenate	274
Methylenomycin B	319
Myodesmone	320
Nagilactone F	321
Noraflavinine	144
β -Panasinsene	322
Parthenin	91

Pentalenene	323
Podorhizol	159
Prostaglandins	89
Pseudoguaianes	73
Pyrethroids	177
Quadrone	324
Quassinoids	58
Sarkomycin	325
Silphinene	326
Steroids	277, 290, 327, 328
Strigol	180
Valerane	118
Vernolepin	329
Zonarol	138

Heterocycles are available by exploitation of this methodology, (148, 296) an area which recently has seen renewed interest. (146, 149, 226, 297-299) MIRC sequences and their variations (137) allow the preparation of cyclopropanes and cyclobutanes, (201) provide a protocol for appending new rings onto a substrate, (300) and allow access to complex polycycles and spirocycles.

6. Experimental Conditions

6.1. Preparation and Handling of Nucleophilic Reagents

The majority of the nucleophiles discussed in this review require in situ preparation because of their high reactivity. Anhydrous solvents, glassware, reagents and transfers, and an inert atmosphere are required. Simple benchtop techniques using routine laboratory glassware, syringes, and cannulae provide sufficient exclusion of air and moisture while minimizing cost and complexity. (330, 331)

Many of the simple nucleophiles are commercially available; frequently those that are not require the use of commercially available organometallics such as Grignards or organolithiums in the preparation process. Degradation of the titer of such reagent solutions occurs with time because of contamination with oxygen or moisture. Freshly prepared solutions of Grignards and organolithiums may vary appreciably in strength because of the inability to precisely control a number of factors, such as temperature of formation and solvent loss. It is strongly recommended that these organometallics be titrated prior to use in any phase of a 1,4 addition. A number of new titration methods are easy and accurate. The nature of the indicator(s) requires only one titration to be performed. (332-336)

Methods also exist for verifying the complete formation of stoichiometric organocuprates. (71) Use of these titration procedures assures the greatest likelihood of avoiding a specious result in the initial step of an attempted tandem vicinal difunctionalization.

6.2. One-Vessel Tandem Vicinal Difunctionalization vs. Vicinal Difunctionalization via a Neutral Intermediate

Before α -alkylation of a conjugate enolate or its trapping as a masked neutral intermediate is investigated, it is best to carry out a proton quench. By examination of the β -addition product, the efficiency of the first step of tandem vicinal difunctionalization can be ascertained clearly. Optimization of the first stage guarantees generation of the maximum amount of conjugate enolate regardless of the eventual pathway of α -functionalization.

The number of examples of one-vessel tandem vicinal difunctionalization greatly outnumbers those via a neutral intermediate. In most instances, recourse to the latter method is made only after variations of the former have failed. (337) This generalization applies particularly for intermolecular α -alkylations. Usually, the following are made to assure that the one-pot difunctionalization occurs: solvent changes, (221, 232) the reactivity of the alkylating agent increased, (118) other nucleophile counterions used, (114) the sequence of the alkylation process altered, (338) and combinations of all of

these.

If these tactics are unsuccessful, trapping of the conjugate enolate as a neutral intermediate is usually performed; the trimethylsilyl enol ether is used most often in this capacity. (337, 339, 340) Purification of the neutral intermediate serves two functions: the opportunity to assess the amount of 1,4 addition and the removal of byproducts that may complicate the α -alkylation step.

Regeneration of the conjugate enolate from its silyl enol ether can be done in liquid ammonia–tetrahydrofuran with lithium amide (64, 339) or in diethyl ether with methyllithium. (4) When compared directly with the one-vessel procedure, the two-step method generally produces the higher yield.

6.3. Solvent

The choice of solvent for tandem vicinal difunctionalization requires striking a balance between a good solvent for 1,4 addition and one that can likewise enhance the α -functionalization. Diethyl ether, in most instances, is the best solvent for the conjugate addition of cuprates; (341) however, it is a poor solvent for enolate alkylation. When only one solvent is used throughout both the conjugate addition and α -alkylation steps, it is tetrahydrofuran. Even though tetrahydrofuran, in some instances, may be disadvantageous for the initial step, (341) it is a better alkylating medium than diethyl ether.

Subsequently, with enone substrates, diethyl ether and tetrahydrofuran have been used with approximately the same frequency for the first step. On the other hand, both steps of the reactions of enoates and enamides are preferentially carried out in tetrahydrofuran.

To obtain maximum yields (since the seminal work of Stork, (26) Boeckman, (232) and Coates and Sandefur (221)), most experimentalists modify the nonpolar medium of conjugate addition. Two general procedures exist. First, after the conjugate addition, solvent is removed and 1,2-dimethoxyethane (DME) is added for the alkylation step; (221) this method has not been exploited to a great extent. The alternative procedure involves altering the structure and reactivity of the conjugate enolate by admixing a polar aprotic solvent such as HMPA in a ratio of 10–20% by volume. (232, 342) The latter protocol has received wider use because of its greater simplicity. Cyclic ureas such as *N,N*-dimethyl-*N,N'*-propyleneurea (DMPU) can be substituted for the animal carcinogen HMPA as cosolvent in the reactions of nucleophiles and bases, (343) and one example of its use in a tandem vicinal difunctionalization is reported. (260) Other polar solvents that have not been utilized routinely as adjuvants include *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (118) and liquid ammonia. (344) Inverse addition, adding the enolate to alkylating agent dissolved in a polar aprotic solvent, increases the yield of desired product in some cases. (114, 338, 345)

It should be emphasized that polar aprotic solvents (donor solvents (341))

generally are deleterious to 1,4 additions (39, 118) and so should not be a part of the reaction medium until that step is complete. Sulfur-stabilized anions (151, 164) are an obvious exception to this generalization; here HMPA is needed to assure the desired 1,4 regioselectivity.

6.4. Temperature

Several patterns are discernible as to the temperatures used in the two steps of vicinal tandem difunctionalization. In keeping with the high lability of the nucleophiles, to maintain regioselectivity, and in order to minimize alkylation of the conjugate enolate with unreacted α , β -unsaturated substrate, the first step is usually carried out at -78 to -30° . The reactions are initiated by adding the substrate to the nucleophile at the lower end of the range, and the reaction temperature then is permitted to rise to allow conjugate enolate formation to occur within a reasonable time (2–4 hours). Obviously, monitoring disappearance of starting material or appearance of β -substituted product makes for an informed decision as to whether or not the reaction temperature needs to be raised.

The conjugate addition is performed on average at lower temperature than the α -alkylation. Frequently, the enolate mixture is re-cooled to -78° prior to adding the adjuvant solvent and the alkylating agent. Care must be exercised during any sampling procedure or addition step to rigorously exclude contaminants such as moisture. Temperatures of -30 to 0° are usually sufficient for alkylations with highly reactive reagents such as methyl iodide and allylic and propargylic bromides. Somewhat less reactive halides (e.g., α -bromoesters (114)) may require room temperature. The heating of reaction mixtures above room temperature usually is reserved for intramolecular alkylations (82) where steric factors neutralize the effect of enolate equilibration that most certainly occurs but goes undetected.

For the most part, the temperatures reported are those of the cooling bath, not those recorded from an internal thermometer. The exothermic nature of both steps of tandem vicinal difunctionalization warrants routine use of the latter protocol if a deeper understanding of these multifaceted processes is to be acquired.

7. Experimental Procedures

In this section, examples are given to highlight the various factors that have been discussed throughout the text. The procedures bring together many of the aspects that require consideration for a tandem vicinal dialkylation protocol to succeed. They have been chosen because they illustrate these principles in detail.

Catalytic organocopper reactions with Grignards and an organolithium are outlined; quenching of the enolates is done in situ, intramolecularly, and via a neutral intermediate. Conjugate addition of a mixed homocuprate followed by an inverse quench is also described. A procedure involving a conjugate enolate derived from a higher-order cuprate, trapped as a silyl enol ether and α -alkylated in the presence of a transition metal catalyst, is detailed.

Examples of noncuprate nucleophiles include an ester enolate initiating an intramolecular ring closure (MIRC), a sulfur-stabilized anion regioselectively undergoing 1,4 addition to an enone followed by in situ α -alkylation, and a Grignard adding to a sulfinyl-activated enone in asymmetric fashion.

7.1.1.1. Methyl

3,3-Dimethyl-6-oxo-2-[5-(trimethylsilyl)-4-pentynyl]cyclohexanecarboxylate (Copper-Catalyzed Conjugate Addition of a Grignard Reagent to a Cyclic Enone Followed by in situ α -Acylation) (79)

To 6.25 g (50 mmol) of 4,4-dimethyl-2-cyclohexen-1-one and 0.5 g (5.6 mmol) of cuprous cyanide in 400 mL of diethyl ether at -23° under argon was added 100 mL (~ 0.75 M in diethyl ether) of 5-trimethylsilyl-4-pentynylmagnesium iodide during 4 hours. Methyl chloroformate (8 mL, 100 mmol) was added and stirring continued for 1 hour at -23° and 0.5 hour at room temperature.

Hydrochloric acid (100 mL, 2.0 M) then was added and the organic phase separated and dried with magnesium sulfate. The solvent was removed and the residue chromatographed on silica gel using 5% diethyl ether–petroleum ether to give methyl

3,3-dimethyl-6-oxo-2-[5-(trimethylsilyl)-4-pentynyl]cyclohexanecarboxylate, 9.66 g (60%). IR 2000, 2140, 1755, 1715, 1660, 1615, 1440, 1280, 1250, 1225, 1205, and 845 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 0.13 (s, 9H), 0.93 (s, 3H), 1.02 (s, 3H), 1.2–2.3 (m, 11H), 3.74 (s, 3H). Anal. Calc. for $\text{C}_{18}\text{H}_{30}\text{O}_3\text{Si}$: C, 67.05; H, 9.4. Found: C, 67.1; H, 9.65.

7.1.1.2. Octahydro-5-methylene-1(2H)-naphthalenone (Lewis Acid–Copper-Catalyzed Conjugate Addition of an Organolithium to 2-Cyclohexen-1-one and Protonation of the Conjugate Enolate Followed by Intramolecular α -Alkylation) (82)

To a cold (-78°) stirred solution of (5-chloro-2-pentenyl)-trimethylstannane (100 mg, 0.37 mmol) in 3.6 mL of dry THF was added a solution of methyllithium in diethyl ether (0.28 mL, 0.41 mmol). The colorless solution was stirred at -78° for 15 minutes. Anhydrous MgBr_2 , (41 mg, 0.4 mmol) was added and the resultant milky solution was stirred for 20 minutes. After successive addition of $\text{CuBr}\cdot\text{DMS}$ (19 mg, 0.09 mmol) and 2-cyclohexen-1-one (0.04 mL, 0.41 mmol), the solution was stirred at -78° for 3 hours. Saturated aqueous ammonium chloride (pH 8) and diethyl ether were added successively and the layers were separated. The aqueous layer was washed twice with ether. The combined ether extracts were washed with saturated aqueous ammonium chloride and dried over anhydrous MgSO_4 . Removal of the solvent gave a colorless oil (81 mg) which was subjected to column chromatography on silica gel (elution with 3:2 petroleum ether–ether). Distillation (air bath temperature $82\text{--}85^{\circ}/0.2$ Torr) of the oil thus obtained provided 60 mg (81%) of 3-(5-chloro-2-pentenyl)cyclohexanone. IR (film) 1700, 1630, 900 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.52–2.48 (series of m, 13H), 3.54 (t, $J = 6$ Hz, 2H), 4.85 (s, 2H); exact mass calculated for $\text{C}_{11}\text{H}_{17}^{35}\text{ClO}$: 200.0968; found: 200.0963.

To a solution of the ketone (105 mg, 0.53 mmol) in 2.6 mL of dry THF at room temperature was added 1.5 mmol of potassium hydride (300 mg, 20% dispersion in mineral oil), and the resultant mixture was stirred at room temperature for 2 hours. Saturated aqueous ammonium chloride was added slowly and the mixture was extracted thoroughly with ether. The combined ether extracts were dried over anhydrous MgSO_4 . Removal of the solvent followed by distillation (air bath temperature $100\text{--}120^{\circ}/23$ Torr) of the residual material provided 69 mg (86%) of a clear oil which consisted of a mixture of bicyclic ketones in a ratio of 1:2. Separation of this mixture by column chromatography on silica gel (10 g, elution with 10:1 petroleum ether–ether) gave 21 mg of *cis*-octahydro-5-methylene-1(2H)-naphthalenone. IR (film) 1700, 1630, 895 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 1.31–2.27 (series of m, 14H), 4.66 (t, $J = 2$ Hz, 1H), 4.69 (s, 1H); exact mass calculated for $\text{C}_{11}\text{H}_{16}\text{O}$: 164.1202; found: 164.1205. There was also obtained 40 mg of *trans*-octahydro-5-methylene-1(2H)-naphthalenone, mp $28\text{--}29^{\circ}$; IR (CHCl_3): 1700, 1635, 890 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 1.20–2.45 (series of m, 14H), 4.70 (s, 1H), 4.75 (s, 1H); exact mass calculated for $\text{C}_{11}\text{H}_{16}\text{O}$: 164.1202; found: 164.1202].

7.1.1.3. (\pm)-2 α , 3 β , 4 α - and (\pm)-2 α , 3 α , 4 β
-2,4-Dimethyl-3-[2-(1,3-dioxan-2-yl)-ethyl]cycloheptanone (Copper-Catalyzed Conjugate Addition, Trapping of the Enolate as a Neutral Equivalent, Solvent Change, and Subsequent α -Alkylation) (91)

A solution of Grignard reagent was prepared from 0.243 g (10.0 mmol) of magnesium turnings and 1.73 g (8.87 mmol) of 2-(2-bromoethyl)-1,3 dioxane in 15 mL of THF. The light-gray Grignard solution (not titrated) was cooled to

-20° and 95.2 mg (0.50 mmol) of copper(I) iodide was added. The reaction mixture was stirred at -20° for 30 minutes and 1.00 g (8.06 mmol) of 4-methyl-2-cyclohepten-1-one in 4 mL of dry THF was added over a 20-minute period to the now black reaction mixture. When the addition was complete, 1.40 mL (1.01 g, 10.0 mmol) of triethylamine and then 1.52 mL (1.30 g, 120 mmol) of chlorotrimethylsilane were added. The reaction mixture was allowed to warm to room temperature over 30 minutes and then was poured into 150 mL of saturated aqueous NaHCO₃ solution and 400 mL of ether. The organic phase was separated, washed with 100 mL of saturated aqueous NaHCO₃ solution and 100 mL of brine, and then dried over MgSO₄.

Removal of solvent in vacuo yielded 2.70 g (9.52 mmol, 118%) of a yellow liquid. TLC analysis (10% ether in hexanes) showed two spots with R_f 0.25 and 0.76, with the latter being UV active. Preparative HPLC separation yielded 876.3 mg (2.81 mmol, 35%) of a colorless liquid that gave a satisfactory combustion analysis: IR (neat) 1663, 1383, 1259 cm⁻¹; ¹H NMR (CCl₄) δ 0.9 (m, 3H), 3.68 (br t, J = 11 Hz, 2H), 4.05 (dd, J = 4 and 12 Hz, 2H), 4.40 (br t, 1H), 4.75 (m, 1H); ¹³C NMR (CDCl₃) *trans* isomer 0.19, 20.4, 21.9, 25.8, 28.0, 32.9, 34.7, 34.9, 35.7, 41.1, 66.7, 102.4, 111.3, 153.7. Anal. Calc. for C₁₇H₃₂O₃Si : C, 65.38; H, 10.25. Found: C, 65.05; H, 10.4.

To a solution of 786.3 mg (2.52 mmol) of *trans* (±)-[(3-[2-(1,3-dioxan-2-yl)ethyl]-4-methyl-1-cyclohepten-1-yl)oxy]trimethylsilane in 5 mL of DME at room temperature was added 2.04 mL of 1.30 M methylolithium in ether (2.65 mmol) over a 2-minute period. The mixture was stirred at room temperature for 45 minutes and then cooled to 5° in an ice bath, and 3.58 g of iodomethane (2.52 mmol) was added rapidly. The mixture was stirred at 5° for 15 minutes and then poured into a mixture of 100 mL of saturated aqueous NaHCO₃ and 180 mL of ether. The organic layer was separated, washed with 100 mL of water and 100 mL of brine, and dried over MgSO₄. TLC analysis (40% ether in hexanes) showed two spots (H₂SO₄ charring) with R_f 0.25 (strong) and 0.32 (weak).

Removal of the solvent in vacuo yielded 683.1 mg (2.71 mmol, 108%) of a yellow liquid. The crude product was purified by column chromatography (40% ether in hexanes) to yield 51.2 mg (0.203 mmol, 8%) of one C-2 epimer (R_f 0.31) and 450.0 mg (1.79 mmol, 71%) of the other C-2 epimer of the title compound. Fraction 1: IR (neat) 1704, 1460, 1380, 1242, 1145 cm⁻¹; ¹H NMR (CCl₄) δ 1.02 (d, J = 7 Hz, 6H), 3.65 (br, t, J = 11 Hz, 2H), 4.04 (dd, J = 5 and 11 Hz, 2H), 4.40 (br t, 1H). Fraction 2: IR (neat) 1702, 1460, 1380, 1242, 1145 cm⁻¹; ¹H NMR (CCl₄) δ 0.91 (d, J = 7 Hz, 3H), 1.03 (d, J = 7 Hz, 3H), 3.65 (br t, J = 11 Hz, 2H), 4.04 (dd, J = 5 and 11 Hz, 2H), 4.40 (br t, 1H); ¹³C NMR (CDCl₃) 15.9, 20.7, 20.8, 25.3, 25.6, 30.6, 33.9, 36.6, 42.5, 46.3, 48.0,

66.6, 102.2, 215.7. Anal. Calc. for C₁₅H₂₆O₃: C, 70.88; H, 10.24. Found: C, 70.71; H, 10.27.

7.1.1.4. Methyl trans-2-(6-Methoxy-2-naphthyl)-5-oxocyclopentaneacetate (Conjugate Addition Using a Mixed Homocuprate and Inverse Quenching of the Conjugate Enolate) (114)

In a dry, argon-purged, round-bottomed flask with a gas inlet and serum stopper was placed 0.065 g (0.5 mmol) of *n*-pentynylcopper. To this was added 0.61 mL (0.5 mmol, 0.82 M in THF) of 6-methoxy-2-naphthylmagnesium bromide via syringe. The mixture was stirred rapidly for 1 hour at room temperature during which time the solution became dark green and homogeneous.

To the (6-methoxy-2-naphthyl)-1-pentynylcoppermagnesium bromide (0.5 mmol) was added 0.05 mL (0.5 mmol) of 2-methyl-2-cyclopenten-1-one. During the course of stirring for 3 hours, the solution turned black but remained homogeneous. To a separate, dry, argon-purged, two-necked, round-bottomed flask fitted with a gas inlet and serum stopper were added 10 mL of dry HMPA and 0.66 mL (5.0 mmol) of ethyl iodoacetate. The enolate solution was diluted with 2.5 mL of dry THF and transferred via syringe to the room-temperature HMPA solution, and stirring was continued for 16 hours. The dark green-black solution became faint yellow over this period. The reaction mixture was then diluted with 10 mL of diethyl ether and saturated aqueous ammonium chloride, and the phases were separated. HPLC analysis indicated no unalkylated material: IR (CHCl₃) 3040 (w), 2945 (s), 1745 (s), 1730 (s), 1640 (s), 1600 (s), 1400 (s), 1380 (m), 1260 (s), 1150 (s), 1010 (m), 880 (m), 850 (m) cm⁻¹; ¹H NMR (CDCl₃) δ 0.62 (s, 3H, C₁₃-CH₃), 1.32 (t, *J* = 7 Hz, 3H, C₂H₅), 2.45 (b, 7H), 3.85 (s, 3H, OCH₃), 4.18 (q, *J* = 7 Hz, 2H, C₂H₅), 7.4 (b, 6H); mass spectrum (70 eV) *m/z* (rel intensity) 340 (M⁺, 5), 295 (M⁺ - 45, 3), 45 (base).

7.1.1.5. tert-Butyl trans-2-Ethoxycarbonylcyclopentaneacetate [Conjugate Addition of an Ester Enolate Followed by Intramolecular Alkylation (MIRC)] (129)

Under a nitrogen atmosphere, to a THF-hexane (1.5 ± 1 mL) solution of lithium diisopropylamide (1.5 mmol) was added a THF (1.5 mL) solution of *tert*-butyl acetate (175 mg, 1.5 mmol) at -78°. After 30 minutes, potassium *tert*-butoxide (169 mg, 1.5 mmol) in THF (2.5 mL) was added and the mixture was stirred for 10 minutes. Ethyl 6-iodo-2-hexenoate, (133 mg, 0.5 mmol) in THF then was added and the reaction was continued for 30 minutes at -78°. Saturated aqueous ammonium chloride was added, and organic materials were extracted with ethyl acetate, dried over Na₂SO₄, and concentrated. Short-path distillation at 105° (0.5 mm Hg) gave *tert*-butyl *trans*-2-ethoxycarbonylcyclopentaneacetate (107 mg, 84%). IR (neat) 1720 cm⁻¹. ¹H NMR (CDCl₃-CCl₄) δ 1.25 (t, *J* = 7 Hz, 3H), 1.43 (s, 9H),

1.6–2.0 (m, 6H), 2.0–2.6 (m, 4H), 4.11 (q, $J = 7$ Hz, 2H); ^{13}C NMR (CDCl_3 - CCl_4) δ 14.2, 24.5, 28.0, 29.9, 32.3, 40.4, 40.5, 49.5, 59.9, 79.7, 171.1, 175.1.

7.1.1.6. (\pm)-2 α , 3 β

-3-(1-Methylthio-2-propenyl)-2-(3-trimethylsilyl-2-propynyl)-cyclopentanone
(Conjugate Addition of a Sulfur-Stabilized Anion Followed by α -Alkylation in situ) (151)

sec-Butyllithium (1.84 M in pentane) was added dropwise to a stirred solution of allyl methyl sulfide (0.49 g, 5.6 mmol) in 20 mL of THF containing 1.0 g (5.6 mmol) of HMPA at -50° until an initial coloration due to the anion persisted in the solution. More *sec*-butyllithium (3.04 mL, 5.6 mmol) then was added and after 10 minutes the temperature of the solution was lowered to -78° . Neat 2-cyclopenten-1-one (0.46 g, 5.6 mmol) was added slowly to keep the temperature of the solution below -70° . The yellow color of the anion disappeared and after 2 minutes (3-iodo-1-propynyl)trimethylsilane (2.52 g, 10.1 mmol) was added dropwise to the reaction mixture at -78° . The temperature of the reaction mixture was raised to -45° during 90 minutes. The reaction was quenched with aqueous ammonium chloride and then worked up to give a pale yellow oil, which was subjected to preparative TLC (SiO_2 , CH_2Cl_2) to yield two fractions. The more polar fraction, R_f 0.5, a pale yellow oil, was a 3:2 diastereomeric mixture of (*E*)-2-(3 ϕ -trimethylsilyl-2-propynyl)-3-(1 2 -methylthio-2 2 -propenyl)-1-cyclopentanone: 2.65 g (75%); IR 2180 (m, C = C), 1750 (s, C = O) cm^{-1} ; ^1H NMR (major diastereomer) δ 0.13 [s, 9H, $\text{Si}(\text{CH}_3)_3$], 1.6–2.7 (m, 8H, H-2, H-3, H-4, H-5, H-1 ϕ), 3.40 (ddd, $J = 9.4, 5.6,$ and 0.5 Hz, 1H, H-1 2), 5.11 (ddd, $J = 16.3, 2.0,$ and 0.5 Hz, 1H, H-3 2), 5.22 (ddd, $J = 10.2, 2.0,$ and 0.2 Hz, 1H, H-3 2), 5.77 (1H, ddd, $J = 16.3, 10.2,$ and 9.5 Hz, H-2 2); ^{13}C NMR δ [q, $\text{Si}(\text{CH}_3)_3$], 14.3 (q, SCH_3), 19.6 (t, C-1 ϕ), 24.2 (t, C-4), 37.6 (t, C-5), 44.2 (d, C-3), 50.5 (d, C-2), 53.3 (d, C-1 2), 86.8 (s, C-3 ϕ), 103.7 (s, C-2 ϕ), 117.9 (t, C-3 2), 137.0 (d, C-2 2), 217.0 (s, C-1); mass spectrum calculated for $\text{C}_{15}\text{H}_{24}\text{OSSi}$ (M^+) m/e 280.1316; found: 280.1306.

The less polar fraction, R_f 0.7, was a mixture of two major diastereomers (3:2) and one minor diastereomer of 3-(1 2 -methylthio-2-propenyl)-2,5-bis[3 ϕ -(trimethylsilyl)-2 ϕ -propynyl]-1-cyclopentanone: 0.32 g (4%); IR 2179 (s, C = C), 1745 (s, C = O) cm^{-1} ; ^1H NMR (major diastereomer) δ 0.14 [s, 18H, $\text{Si}(\text{CH}_3)_3$], 1.8–2.8 (m, 9H, H-2, H-3, H-4, H-5, H-1 ϕ), 2.02 (s, 3H, SCH_3), 3.29 (ddd, $J = 9.5$ and 6.1 Hz, 1H, H-1 2), 5.09 (ddd, 1H, 2.0, and 0.3 Hz, $J = 16.4$, H-3 2), 5.15 (ddd, $J = 10.1, 2.0,$ and 0.2 Hz, 1H, H-3 2), 5.72 (ddd, $J = 16.4, 10.1,$ and 9.4 Hz, 1H, H-2 2); ^{13}C NMR δ 0.06 [q, $\text{Si}(\text{CH}_3)_3$], 14.2 (q, SCH_3), 20.3 (t, C-1 ϕ), 28.6 (t, C-4), 41.8 (d, C-3), 45.5 (d, C-5), 50.9 (d, C-2), 55.2 (d, C-1 2), 86.2 (s, C-1 ϕ), 104.2 (s, C-2 ϕ), 117.8 (t, C-3 2), 135.6 (d, C-2 2), 217.3 (s, C-1); mass spectrum calculated for $\text{C}_{21}\text{H}_{34}\text{OSSi}$ (M^+) m/z 390.1868; found: 390.1867.

7.1.1.7. (2*R*, 3*R*, *S*_s)- and (2*S*, 3*R*, *S*_s)-3-(6-Methoxy-2-naphthyl)-2-methyl-2-(4-methylphenyl)sulfinylcyclopentanone (Conjugate Addition of a Grignard to an Activated Enone Involving Asymmetric Induction) (192)

A flame-dried, 25-mL, 2-necked, round-bottomed flask fitted with serum cap, 3-way stopcock, and magnetic stirring bar and containing 5 mL of anhydrous THF was charged with 6-methoxy-2-naphthylmagnesium bromide (300 mL, 0.54 mmol) and cooled to -78° . After the Grignard reagent had cooled, (S)-[(4-methylphenyl)sulfinyl]-2-cyclopenten-1-one (107 mg, 0.49 mmol) in 2 mL of THF was added dropwise via syringe. After 20 minutes at -78° , the cold bath was removed to allow warming to room temperature. The THF was removed under reduced pressure (20 mm Hg) at 20° . The resultant semisolid was treated sequentially with methyl iodide (5 mL) and dry *N*-methylpyrrolidinone (4 mL). The homogeneous reaction mixture was stirred at room temperature overnight (20° , 12 hours). The crude product was concentrated under vacuum (20 to 0.1 mm Hg) and purified by preparative TLC (SiO₂, 20 cm × 20 cm × 1500 mm, 1:1:1 pentane/ether/methylene chloride, *R*_f 0.33) to give a 2:1 mixture of (2*R*, 3*R*, *S*_s)-*cis*-3-(6-methoxy-2-naphthalenyl)-2-methyl-2-[(4-methylphenyl)sulfinyl]cyclopentanone and (2*S*, 3*R*, *S*_s)-3-(6-methoxy-2-naphthalenyl)-2-methyl-2-[(4-methylphenyl)sulfinyl]cyclopentanone (149 mg, 78%) as a semisolid. ¹H NMR (CDCl₃) δ 0.99 (s, 2H), 1.2 (s, 1H), 2.40 (s, 3H), 1.8–3.90 (br m, 5H), 3.95 (s, 3H), 7.0–8.1 (m, 10H); IR (CHCl₃), 1730 (s), 1601 (s), 140 (s). Anal. Calc. for C₂₉H₂₉O₃S : C, 73.44; H, 6.16; S, 8.17. Found: C, 73.50; H, 6.19; S, 7.91.

7.1.1.8. Methyl (±)-(Z)-1 α ,2 β -7-(Ethenyl-5-oxocyclopentyl)-5-heptenoate (Conjugate Addition of a Higher-Order Cuprate, Trapping of the Conjugate Enolate as the Silyl Enol Ether, and α -Alkylation Mediated by a Transition Metal Catalyst) (86)

[(3-Ethenyl-1-cyclopenten-1-yl)oxy]trimethylsilane was prepared by the method of Lipshutz, Wilhelm, and Kozlowski (345a) using CuCN (2.60 g, 30 mmol) azeotropically dried with 15 mL of toluene at room temperature under vacuum, 25 mL (60 mmol) of 2.4 M vinyl lithium, 1.3 mL (1.27 g, 15 mmol) of 2-cyclopenten-1-one, and trimethylsilyl chloride (6.3 mL, 5.43 g, 50 mmol); yield 2.35 g (86%), bp 33–35° (0.15 mm); IR (neat) 1640 (s), 1345 (s), 1265 (s), 1250 (s), 1230 (s), 930 (s), 910 (s), 850 (br s) cm⁻¹; ¹H NMR (CDCl₃, Me₄Si) δ 0.20 (s, 9H), 1.2–2.5 (m, 4H), 3.0–3.4 (m, 1H), 4.5–5.1 (m, 3H), 5.5–6.0 (m, 1H). ¹³C NMR (CDCl₃, Me₄Si) δ 0.45, 28.46, 32.90, 48.50, 104.33, 111.57, 143.25, 155.48. No ¹³C NMR signals assignable to the stereoisomer were detected. Its purity by GLC was ~97%.

To a solution of 0.36 g (2 mmol) of [(3-ethenyl-1-cyclopenten-1-yl)-oxy]trimethylsilane in 5 mL of THF was added dropwise 1 mL (2.4 mmol) of 2.4 M *n*-C₄H₉Li at 0°. After 10 minutes the

mixture was cooled to -78° , and 4 mL (4 mmol) of 1 M $\text{B}(\text{C}_2\text{H}_5)_3$ in THF was added. The resultant mixture was warmed to 0° over 20 minutes, and a solution of 0.40 g (2 mmol) of methyl (*Z*)-7-acetoxy-5-heptanoate and 0.02 g (0.02 mmol) of $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_4]$ in 5 mL of THF was added. After the mixture had been stirred for 2 hours at room temperature, it was quenched with 12 mL of 3 N HCl and extracted with 3×10 mL ether. The extract was washed with aqueous NaHCO_3 , dried over MgSO_4 , concentrated, and passed through a silica gel column (60–200 mesh, *n*-hexane) to remove Pd compounds. Concentration and distillation gave 0.33 g (66%) of methyl (\pm)-(*Z*)-1 α , 2 β -7-(ethenyl-5-oxocyclopentyl)-5-heptenoate: bp $120\text{--}123^{\circ}\text{C}$ (0.2 mm Hg); IR (neat) 1730 (unresolved bands, s), 1640 (w), 1430 (m), 1155 (s), 985 (m), 910 (m) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.1–2.8 (m, 14*H*), 3.6 (s, 3*H*), 4.9–5.5 (m, 4*H*), 5.6–6.1 (m, 1*H*); ^{13}C NMR (CDCl_3) δ 24.59, 26.32, 27.31, 32.88, 37.09, 45.71, 50.71, 53.92, 114.60, 127.09, 130.05, 140.84, 172.70, 216.34. The purity of the product by GLC was ~90% with one unidentified signal having a shorter retention time.

8. Tabular Survey

8.1. Introduction and Guide to Tables

The tabular survey covers examples abstracted from the literature from 1959 through 1986 and is organized according to whether the difunctionalization is a direct sequence with conjugate enolate α -functionalization proceeding in situ (a “one-pot” sequence, Tables I–III) or is an indirect sequence, proceeding through a neutral intermediate conjugate enolate equivalent (a “two-pot” sequence, Tables IV and V). Each table is organized according to the type of α , β -unsaturated carbonyl substrate used (ketones, aldehydes, esters, or amides; cyclic or acyclic) and the number of carbons in the substrate. Aldehydes, ketones, and amides are listed according to total carbon count; carboxylic esters in Tables II and V are listed according to the carbon count of the parent carboxylic acid. Substrates are classified as cyclic only if they are named as 2-cycloalkenones; otherwise, they are considered acyclic.

Identities of the Michael donor, or nucleophilic reagent, and the enolate quenching reagent are listed along with general conditions of the reaction sequence. The conditions indicated should not be considered to be in sufficient detail for duplication of the reaction; the reader is advised to refer to the original experimental details of the reference(s) to determine how the sequence should be performed.

Stereochemical information for the reactants and the products is provided when available, and generally the yields recorded are isolated chemical yields of the products for the entire reaction sequence. Reactions are run in diethyl ether unless noted otherwise, and temperatures are reported in degrees Celsius.

The following abbreviations have been used to facilitate tabulation of the data:

A	proton-quenched adduct isolated as neutral intermediate
acac	acetylacetonate
B	enol acetate isolated as neutral intermediate
cat.	catalytic amount
DBU	1,8-diazabicyclo[4.3.0]undec-7-ene
DMAP	4-(dimethylamino)pyridine
DME	1,2-dimethoxyethane
DMF	<i>N,N</i> -dimethylformamide
DMS	dimethyl sulfide

DMSO	dimethyl sulfoxide
eq	equivalents
g	gas
HMPA	hexamethylphosphorictriamide
l	liquid
LDA	lithium diisopropylamide
LHMDS	lithium 1,1,1,3,3,3-hexamethyldisilazide
LICA	lithium isopropylcyclohexylamide
LTMP	lithium 2,2,6,6-tetramethylpiperidide
<i>m</i> -CPBA	<i>m</i> -chloroperbenzoic acid
NMP	<i>N</i> -methylpyrrolidinone
[O]	oxidation
OAc	acetoxy
rt	room temperature
TASF	tris(dimethylamino)sulfonium difluorotrimethylsiliconate
TBAF	tetrabutylammonium fluoride
TBDSO	<i>tert</i> -butyldimethylsilyloxy
THF	tetrahydrofuran
THP	2-tetrahydropyranyl
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
Ts	<i>p</i> -toluenesulfonyl
X	unspecified halogen

Table I. α , β -Unsaturated Aldehydes and Ketones

[View PDF](#)

Table II. α , β -Unsaturated Esters and Lactones

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Table III. α , β -Unsaturated Amides and Thioamides

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Table IV. α , β -Unsaturated Ketones via Neutral Intermediates

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Table V. α , β -Unsaturated Esters via Neutral Intermediates

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Table VI. Miscellaneous Substrates

[View PDF](#)

Table I. Aldehydes and Ketones—Addenda

[View PDF](#)

Table II. Esters and Lactones—Addenda

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Table V. Esters—Addenda

[View PDF](#)

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES

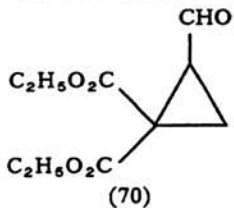
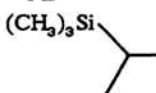
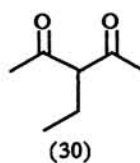
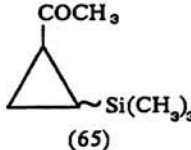
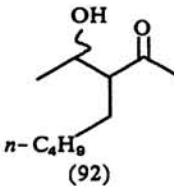
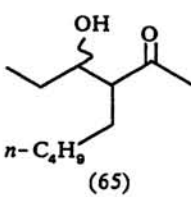
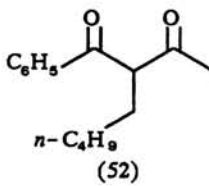
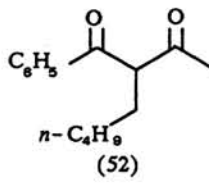
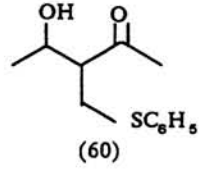
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
3	$\text{CH}_2=\text{CHCHO}$	$(\text{C}_2\text{H}_5\text{O}_2\text{C})_2\text{CHBr}$, NaOC_2H_5 , $\text{C}_2\text{H}_5\text{OH}$, 5°	Intramolecular	 (70)	216
4	$\text{CH}_2=\text{CHCOCH}_3$	$(\text{CH}_3)_2\text{CuLi}$, $(n\text{-C}_3\text{H}_7)_2\text{O}$, 1 h $(\text{CH}_3)_3\text{Si}$  Li, THF, $(\text{CH}_3)_2\text{S}^+ \Gamma^-$ -30° to 15°	CH_3COCl , rt, 1 h Intramolecular	 (30)  (65)	272 157
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, -78°	CH_3CHO , 0° , ZnCl_2	 $n\text{-C}_4\text{H}_9$ (92)	220
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, -78°	$\text{C}_2\text{H}_5\text{CHO}$, 0° , ZnCl_2	 $n\text{-C}_4\text{H}_9$ (65)	220
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi} \cdot (n\text{-C}_4\text{H}_9)_3\text{P}$, -78° , 1 h	$\text{C}_6\text{H}_5\text{COCl}$, HMPA	 $n\text{-C}_4\text{H}_9$ (52)	112
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi} \cdot (n\text{-C}_4\text{H}_9)_3\text{P}$, -78° , 30 min	$\text{C}_6\text{H}_5\text{COCl}$, HMPA	 $n\text{-C}_4\text{H}_9$ (52)	284
		$(\text{CH}_3)_2\text{AlSC}_6\text{H}_5$, CH_2Cl_2 , -78°	CH_3CHO , THF	 (60)	204

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

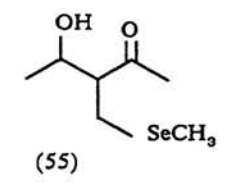
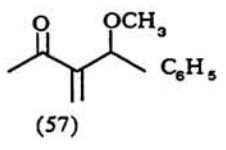
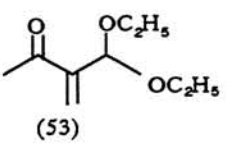
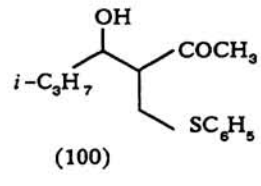
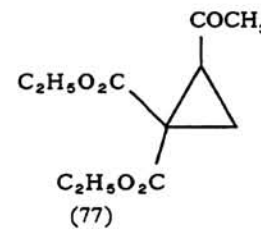
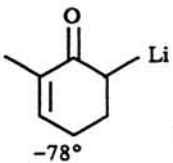
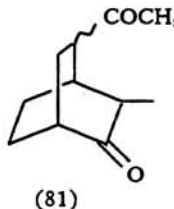
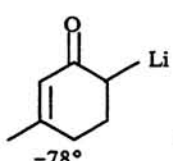
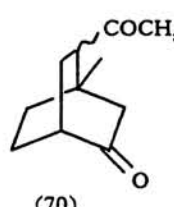
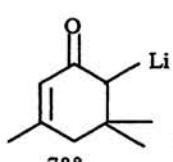
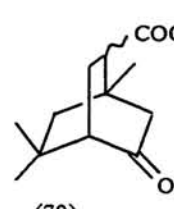
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
		$(\text{CH}_3)_2\text{AlSeCH}_3$, CH_2Cl_2 , -78°	CH_3CHO , THF	 (55)	204
		$(\text{CH}_3)_3\text{SiSeC}_6\text{H}_5$, cat. $(\text{CH}_3)_3\text{SiO}_2\text{CCF}_3$, CH_2Cl_2 , -78°	1) $\text{C}_6\text{H}_5\text{CH}(\text{OCH}_3)_2$ 2) [O]	 (57)	205
		$(\text{CH}_3)_3\text{SiSeC}_6\text{H}_5$, cat. $(\text{CH}_3)_3\text{SiO}_2\text{CCF}_3$, CH_2Cl_2 , -78°	1) $\text{HC}(\text{OC}_2\text{H}_5)_3$ 2) [O]	 (53)	205
		$\text{C}_6\text{H}_5\text{SMgI}$, $(\text{C}_2\text{H}_5)_2\text{O}$, hexane, 0°	$i\text{-C}_3\text{H}_7\text{CHO}$	 (100)	145
		$(\text{C}_2\text{H}_5\text{O}_2\text{C})_2\text{CHBr}$, NaOC_2H_5 , $\text{C}_2\text{H}_5\text{OH}$, 5°	Intramolecular	 (77)	216
	 -78°	, THF,	Intramolecular	 (81)	138
	 -78°	, THF,	Intramolecular	 (70)	138
	 -78°	, THF,	Intramolecular	 (70)	138

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

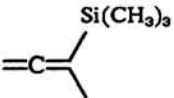
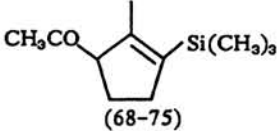
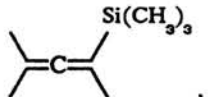
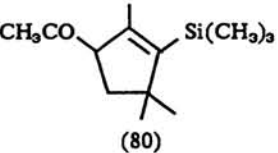
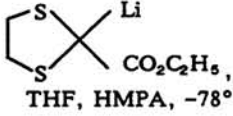
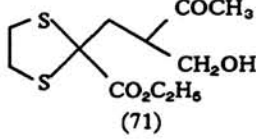
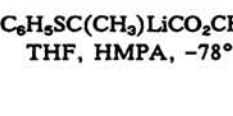
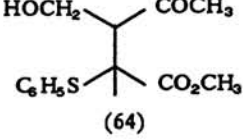
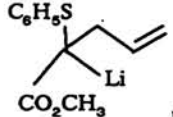
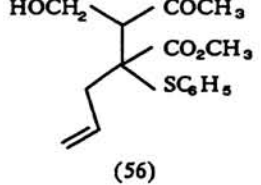

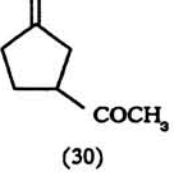
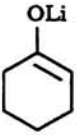
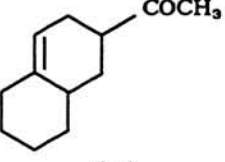
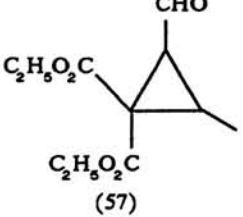
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
		$\text{TiCl}_4, \text{CH}_2\text{Cl}_2, -78^\circ$	Intramolecular	 (68-75)	214
		$\text{TiCl}_4, \text{CH}_2\text{Cl}_2, -78^\circ$	Intramolecular	 (80)	214
		$\text{CO}_2\text{C}_2\text{H}_5, \text{THF, HMPA, } -78^\circ$	$\text{CH}_2\text{O}, -78^\circ$	 (71)	222
		$\text{C}_6\text{H}_5\text{SC}(\text{CH}_3)\text{LiCO}_2\text{CH}_3, \text{THF, HMPA, } -78^\circ$	$\text{CH}_2\text{O}, -78^\circ$	 (64)	222
		$\text{CO}_2\text{CH}_3, \text{THF, HMPA, } -78^\circ$	$\text{CH}_2\text{O}, -78^\circ$	 (56)	222
		$\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4, \text{toluene, } 78^\circ$	Intramolecular	 (30)	215
			1) $(\text{C}_6\text{H}_5)_3\text{B}$ 2) $\text{CH}_2=\text{CHP}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	 (21)	143
	<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHCHO}$	$(\text{C}_2\text{H}_5\text{O}_2\text{C})_2\text{CHBr}, \text{NaOC}_2\text{H}_5, \text{C}_2\text{H}_5\text{OH}, 5^\circ, \text{overnight}$	Intramolecular	 (57)	216

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

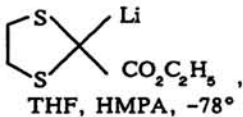
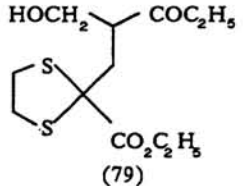
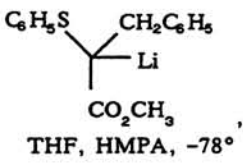
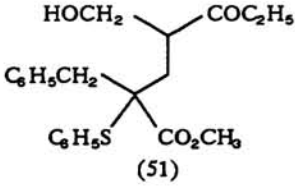
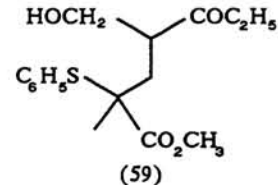
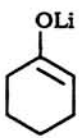
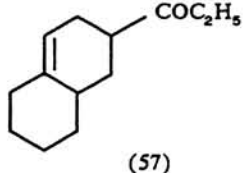
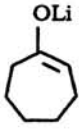
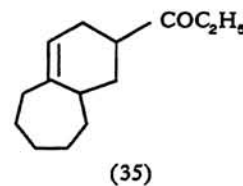
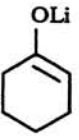
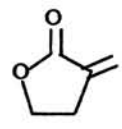
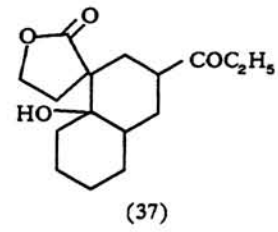
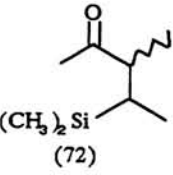
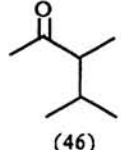
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
5	$\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$	 THF, HMPA, -78°	CH_2O , -78°	 (79)	222
		 THF, HMPA, -78°	CH_2O , -78°	 (51)	222
		$\text{C}_6\text{H}_5\text{SC}(\text{CH}_3)\text{LiCO}_2\text{CH}_3$, THF, HMPA, -78°	CH_2O , -78°	 (59)	222
			1) $(\text{C}_2\text{H}_5)_3\text{B}$ 2) $\text{CH}_2=\text{CHP}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	 (57)	143
			1) $(\text{C}_2\text{H}_5)_3\text{B}$ 2) $\text{CH}_2=\text{CHP}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	 (35)	143
				 (37)	143
	$(E)\text{-CH}_3\text{CH}=\text{CHCOCH}_3$	$[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{CuLi}$, THF, -23°	CH_3I , HMPA	 (72)	63
		$(\text{CH}_3)_2\text{CuLi}$, 0°	CH_3I , DME	 (46)	221

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

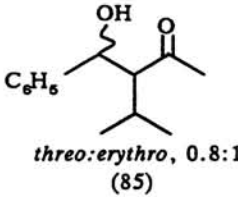
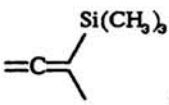
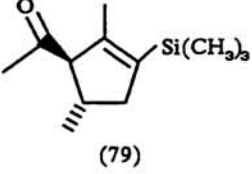
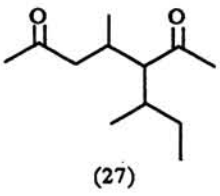
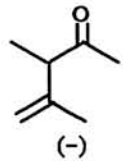

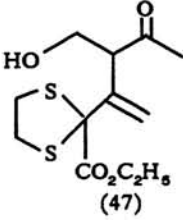
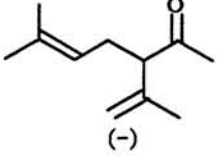
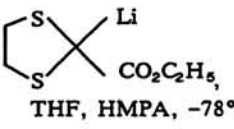
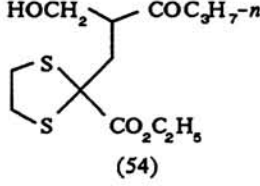
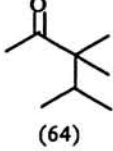
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
304		$(\text{CH}_3)_2\text{CuLi}$, -78°	$\text{C}_6\text{H}_5\text{CHO}$, ZnCl_2	 <i>threo:erythro</i> , 0.8:1 (85)	220
		$\text{TiCl}_4, \text{CH}_2\text{Cl}_2, -78^\circ$	Intramolecular	 (79)	214
		$\text{C}_2\text{H}_5\text{MgBr}$, CuCl , (-)-sparteine	Self	 (27)	18
	$\text{CH}_2=\text{C}=\text{CHCOCH}_3$	$(\text{CH}_3)_2\text{CuLi}$, -15°	CH_3I , DME, -30°	 (-)	255
		 $\text{CO}_2\text{C}_2\text{H}_5$, THF, HMPA, -78°	CH_2O , -78°	 (47)	222
305		$(\text{CH}_3)_2\text{CuLi}$, -15°	$\text{BrCH}_2\text{CH}=\text{C}(\text{CH}_3)_2$, DME, -30°	 (-)	255
6	$\text{CH}_2=\text{CHCO}_3\text{H}_7-n$	 $\text{CO}_2\text{C}_2\text{H}_5$, THF, HMPA, -78°	CH_2O , -78°	 (54)	222
	$(E)\text{-CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{COCH}_3$	$(\text{CH}_3)_2\text{CuLi}$, 0°	CH_3I , DME	 (64)	221

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

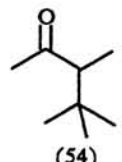
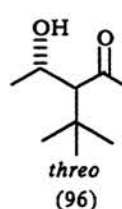
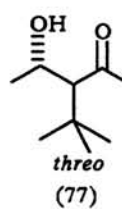
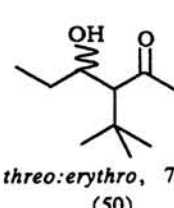
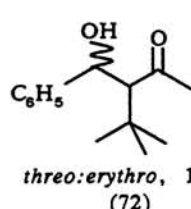
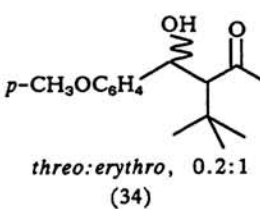
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
	$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3^a$	$(\text{CH}_3)_2\text{CuLi}$, 0°	CH_3I , DME	 (54)	221
		$(\text{CH}_3)_2\text{CuLi}$, -78°	CH_3CHO , 10 eq ZnCl_2	 <i>threo</i> (96)	220 234
		$(\text{CH}_3)_2\text{CuLi}$, -78°	CH_3CHO , 1 eq ZnCl_2	 <i>threo</i> (77)	220
		$(\text{CH}_3)_2\text{CuLi}$, -78°	$\text{C}_2\text{H}_5\text{CHO}$, ZnCl_2	 <i>threo:erythro</i> , 7.4:1 (50)	220
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{C}_6\text{H}_5\text{CHO}$, ZnCl_2	 <i>threo:erythro</i> , 1.0:1 (72)	220
				”	
		$(\text{CH}_3)_2\text{CuLi}$, -78°	$\text{C}_6\text{H}_5\text{CHO}$, ZnCl_2	<i>threo:erythro</i> , 2.0:1 (66)	220
		$(\text{CH}_3)_2\text{CuLi}$, -78°	<i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4\text{CHO}$, ZnCl_2	 <i>threo:erythro</i> , 0.2:1 (34)	220

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

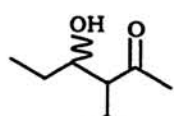
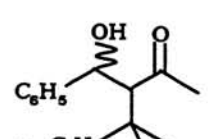
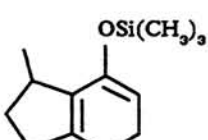
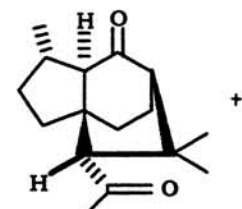
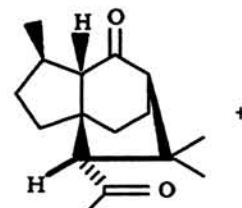
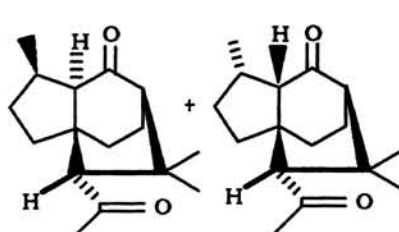
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$p\text{-CH}_3\text{OC}_6\text{H}_4\text{CHO}$, ZnCl_2	” <i>threo:erythro</i> , 1.8:1 (46)	220
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, 0°	$\text{C}_2\text{H}_5\text{CHO}$, ZnCl_2	 <i>n</i> - C_4H_9 <i>threo:erythro</i> , 2.5:1 (93)	220
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, -78°	$\text{C}_2\text{H}_5\text{CHO}$, ZnCl_2	” <i>threo:erythro</i> , 5.5:1 (52)	220
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, -78°	$\text{C}_2\text{H}_5\text{CHO}$, ZnCl_2	 C_6H_5 <i>n</i> - C_4H_9 <i>threo:erythro</i> , 0.8:1 (85)	220
		$\text{TiCl}_4, \text{CH}_2\text{Cl}_2, -78^\circ$ to -40°	Intramolecular	 (21)	295
				 (43)	
				 (17)	

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

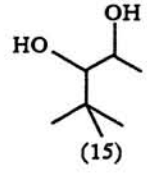
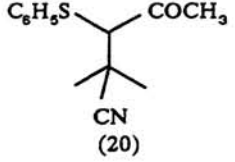
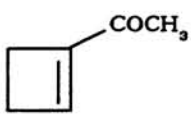
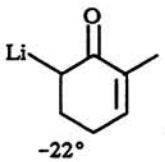
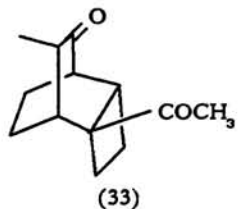
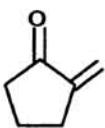
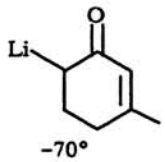
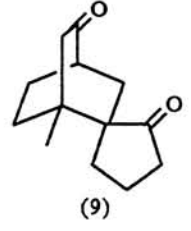
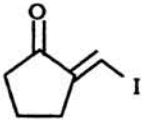
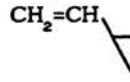
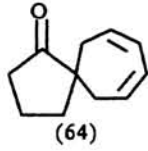
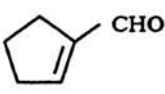
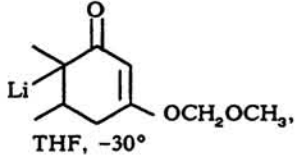
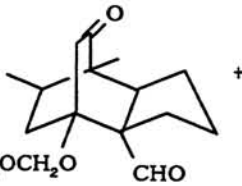
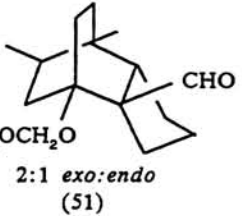
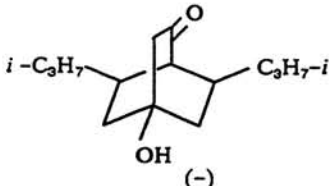
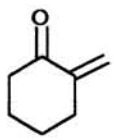
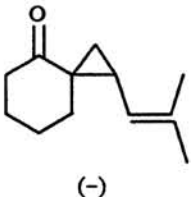
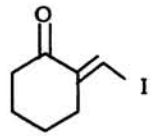

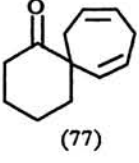
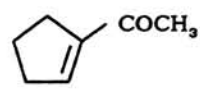
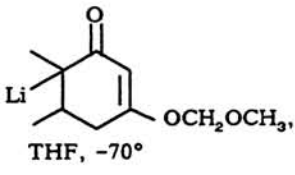
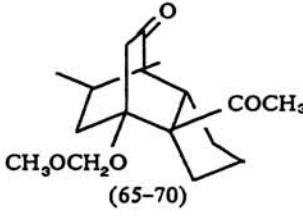
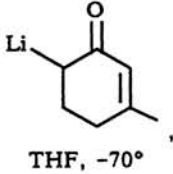
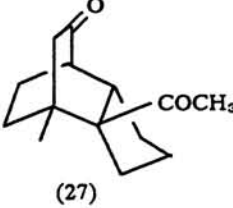
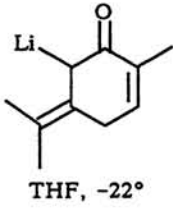
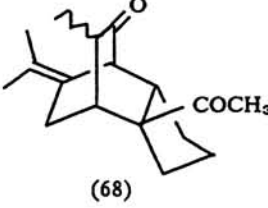
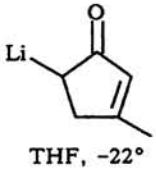
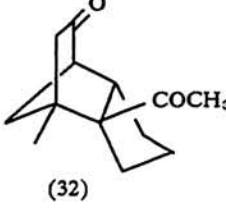
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
310		$(\text{CH}_3)_2\text{CuLi}$, -10°	1) BH_3 , THF 2) alkaline H_2O_2	 (15)	346
		$(\text{C}_2\text{H}_5)_2\text{AlCN}$	$\text{C}_6\text{H}_5\text{SCl}$	 (20)	182
		 -22° , THF,	Intramolecular	 (33)	218
		 -70° , THF,	Intramolecular	 (9)	218
		$\text{CH}_2=\text{CH}$ -  - $\text{Cu}(\text{SC}_6\text{H}_5)_2\text{Li}$	180° , intramolecular	 (64)	121
311		 THF, -30°	Intramolecular	 +  2:1 <i>exo:endo</i> (51)	218

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.	
Section A: Acyclic Substrates						
312	7	$(E)\text{-}i\text{-C}_3\text{H}_7\text{CH=CHCOCH}_3$	$(E)\text{-}i\text{-C}_3\text{H}_7\text{CH=CHCOCH}_3$, Ba(OH)_2	Intramolecular	 (-)	126
			$(\text{C}_6\text{H}_5)_3\text{P=CHCH}_2\text{CH}_3$, 25°	Intramolecular	 (-)	171
			$\text{CH}_2=\text{CH}$  $\text{Cu(SC}_6\text{H}_5)_2\text{Li}$	180°, Intramolecular	 (77)	121
			 THF, -70°	Intramolecular	 (65-70)	218
		 THF, -70°		Intramolecular	 (27)	218
		 THF, -22°		Intramolecular	 (68)	218
		 THF, -22°		Intramolecular	 (32)	218

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TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
314		Li THF, -22°	Intramolecular		218
		Li THF, -22°	Intramolecular		218
		COCH ₂ Li THF, -70°	Intramolecular		218
8		(CH ₃) ₃ Si Li (CH ₃) ₂ S ₂ I ₋ THF, -30° to 15°	Intramolecular		157
		CH ₃ O ₂ C Cu(CH ₃)Li	Intramolecular		110
315		Si(CH ₃) ₃ TiCl ₄ CH ₂ Cl ₂ , -78°	Intramolecular		214
		Li OCH ₂ OCH ₃ THF, -70°	Intramolecular		218
		TsCH ₂ CN, cat. NaOC ₂ H ₅ , C ₂ H ₅ OH	Intramolecular		188

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

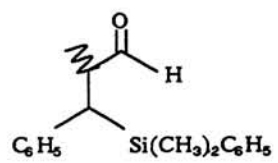
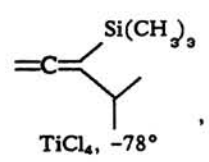
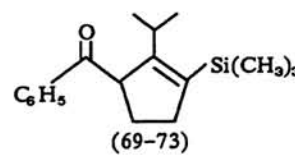
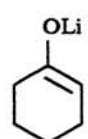
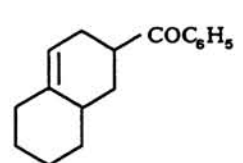
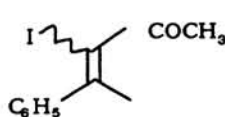
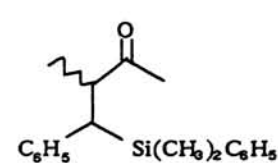
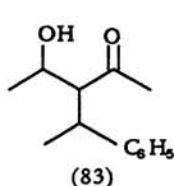
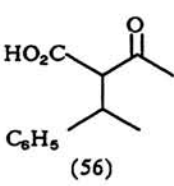
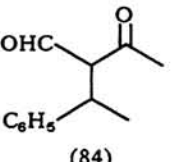
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.	
Section A: Acyclic Substrates						
9	<i>trans</i> -C ₆ H ₅ CH=CHCHO	[C ₆ H ₅ (CH ₃) ₂ Si] ₂ CuLi	CH ₃ I	 <i>threo:erythro</i> , 12:1 (74)	102	
316	CH ₂ =CHCOC ₆ H ₅	 TiCl ₄ , -78°	CH ₂ Cl ₂	Intramolecular	 (69-73)	214
				1) (C ₂ H ₅) ₃ B 2) CH ₂ =CHP ⁺ (C ₆ H ₅) ₃ Br ⁻	 (44)	143
	C ₆ H ₅ C≡CCOCH ₃	1) (CH ₃) ₂ CuLi, -80° 2) CH ₃ Li, -80°	I ₂		62:38 <i>cis:trans</i> (-)	250
10	(<i>E</i>)-C ₆ H ₅ CH=CHCOCH ₃ ^a	[C ₆ H ₅ (CH ₃) ₂ Si] ₂ CuLi	CH ₃ I	 <i>threo:erythro</i> , 49:1 (57)	102	
317		(CH ₃) ₂ CuLi, -78°	CH ₃ CHO, ZnCl ₂	 (83)	220	
		(CH ₃) ₂ CuLi, 0°	CO ₂ (g), rt	 (56)	220	
		(CH ₃) ₂ CuLi, 0°	C ₂ H ₅ O ₂ CH	 (84)	220	

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

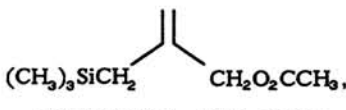
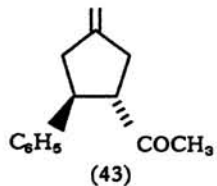
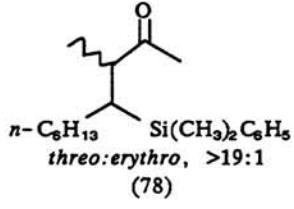
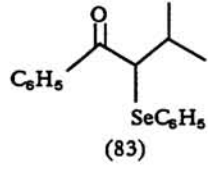
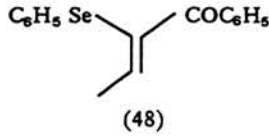
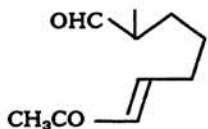
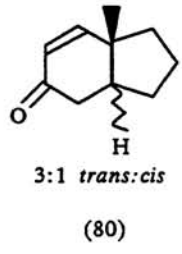
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
		Intramolecular Pd[P(C ₆ H ₅) ₃] ₄ , THF, reflux		 (43)	215
318	(<i>E</i>)- <i>n</i> -C ₈ H ₁₃ CH=CHCOCH ₃	[C ₆ H ₅ (CH ₃) ₂ Si] ₂ CuLi	CH ₃ I	 <i>threo:erythro</i> , >19:1 (78)	102
	(<i>E</i>)-CH ₃ CH=CHCOC ₆ H ₅ ^a	(CH ₃) ₂ CuLi, -40°	C ₆ H ₅ SeBr, (C ₆ H ₅) ₂ Se ₂	 (83)	347 348
		LDA, THF, 0°	C ₆ H ₅ SeBr	 (48)	203
		1) cat. NaOCH ₃ , CH ₃ OH 2) NaOCH ₃	Intramolecular	 3:1 <i>trans:cis</i> (80)	293
		KOH, CH ₃ OH	Intramolecular	2:1 <i>trans:cis</i> (-)	293
319		LiOH, CH ₃ OH	Intramolecular	4:1 <i>trans:cis</i> (-)	293
		1) Zr(OC ₂ H ₇) ₄ , C ₆ H ₆ , rt, 1 h 2) LiOH, CH ₃ OH 3) DMAP, CH ₂ Cl ₂ , (CF ₃ CO) ₂ O, DBU, -40°; then 0°	Intramolecular	40:1 <i>trans:cis</i> (90)	293

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
320 11		$(\text{CH}_3)_2\text{CuLi}$, -78°	Intramolecular THF/HCl, reflux		349
		$(\text{CH}_3)_2\text{CuLi}$, 0°	CH_3I , DME		221
	$(E)\text{-CH}_3\text{CH=CHCOCH}_2\text{C}_6\text{H}_5$	$(\text{CH}_3)_2\text{CuLi}$, -78°	CH_3CHO , ZnCl_2		220 234
		$(\text{CH}_3)_2\text{CuLi}$, -60° , 90 min; then 0° , 60 min	Intramolecular		350
		$(\text{CH}_3)_2\text{AlSC}_6\text{H}_5$, CH_2Cl_2 , -78° , 15 min	Intramolecular		204
321		$(\text{CH}_3)_3\text{SiC}\equiv\text{CCH}_2\text{MgBr}$, cat. $\text{CuBr} \cdot \text{DMS}$, THF, $(\text{C}_2\text{H}_5)_2\text{O}$, -78° , 5 h; -78° to 0° , 2 h; then 0° , 15 min	CH_3I , HMPA		311
		$(\text{CH}_3)_3\text{SiC}\equiv\text{CCH}_2\text{MgBr}$, $\text{CuBr} \cdot \text{DMS}$	CH_3I , HMPA	" (-)	351

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

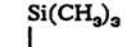
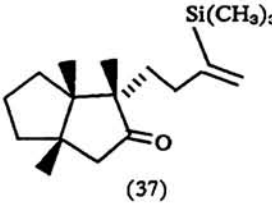
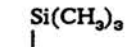
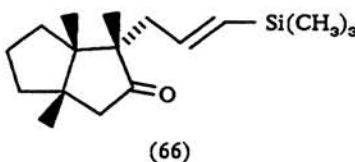
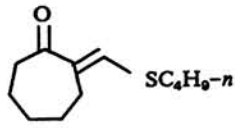
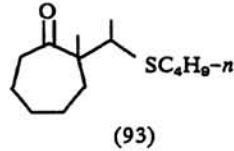
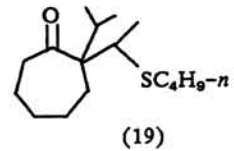
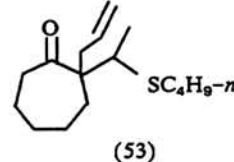
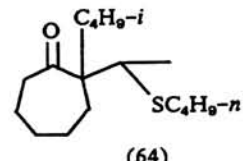
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
		MgBr, cat. CuBr • DMS, -78°, 5 h; -78° to 0°, 2 h; then 0°, 15 min	CH ₃ I, HMPA, rt	 (37)	311
		MgBr, CuBr • DMS	CH ₃ I, HMPA	" (40)	351
		(<i>E</i>)-(CH ₃) ₃ SiCH=CHMgBr, cat. CuBr • DMS, -78°, 5 h; -78° to 0°, 2 h; then 0°, 15 min	CH ₃ I, HMPA	 (66)	311
		(<i>E</i>)-(CH ₃) ₃ SiCH=CHMgBr, CuBr • DMS	CH ₃ I, HMPA	" (66)	351
12		(CH ₃) ₂ CuLi, 0°	CH ₃ I, DME	 (93)	221
		(CH ₃) ₂ CuLi, 0°	<i>i</i> -C ₃ H ₇ I, DME	 (19)	221
		(CH ₃) ₂ CuLi, 0°	CH ₂ =CHCH ₂ Br, DME	 (53)	221
		(CH ₃) ₂ CuLi, 0°	<i>i</i> -C ₄ H ₉ I, DME	 (64)	221

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

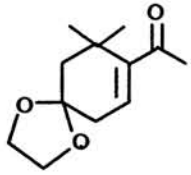
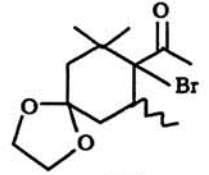
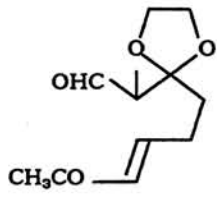
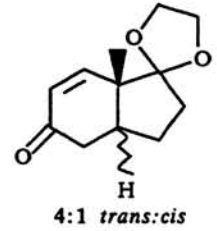
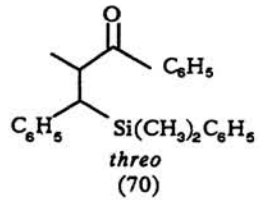
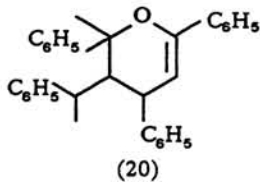
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
		$(\text{CH}_3)_2\text{CuLi}$, 0°	Br_2 , C_6H_6 -40° to 0°	 (99)	308
		LiOH , CH_3OH	Intramolecular	 4:1 <i>trans:cis</i> (-)	293
		$\text{Mg}(\text{OCH}_3)_2$, CH_3OH	Intramolecular	12:1 <i>trans:cis</i> (-)	293
		$\text{Ca}(\text{OCH}_3)_2$, CH_3OH	Intramolecular	10:1 <i>trans:cis</i> (-)	293
		$\text{Ba}(\text{OH})_2$, CH_3OH	Intramolecular	4:1 <i>trans:cis</i> (-)	293
		$\text{Zr}(\text{OC}_3\text{H}_7)_4$	Intramolecular	25:1 <i>trans:cis</i> (-)	293
15	$(E)\text{-C}_6\text{H}_5\text{CH=CHCOC}_6\text{H}_5^a$	$[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{CuLi}$	CH_3I	 <i>threo</i> (70)	102
		CH_3MgI	Self	 (20)	19

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref
Section A: Acyclic Substrates					
			$\text{CH}_2=\text{CHP}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	 (35)	143
326		$(\text{CH}_3)_3\text{SiCH}_2$, CH_2COCH_3 , $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, toluene, 115°	Intramolecular	 (85)	215
16		 DME, -78°	Intramolecular	 (25)	352
				 4:1 mixture of isomers (15)	
327		 -78° to 25°	Intramolecular	 (30)	144
		$[\text{CH}_2=\text{CH}(\text{CH}_2)_3]_2\text{CuLi}$, DMS, $(\text{C}_2\text{H}_5)_2\text{O}$, THF	CH_3I	 (33)	217

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
18		$(C_6H_5)_3P=CH_2$, rt; xylene, 120°	Intramolecular	 (41)	172
23		CH_3MgX , THF, 9 mol % $Cu(O_2CCH_3)_2$	CH_3I , reflux		78
		$C_6H_5CH_2MgX$, THF, 9 mol % $Cu(O_2CCH_3)_2$	CH_3I , reflux	 (43)	78
25		CH_3Li , THF, -78° to 25°	$n-C_4H_9I$	 (83)	197
		$CH_2=CHLi$, THF, -78° to 25°	CH_3I	 (90)	197
		 , THF, -78° to 25°	CH_3I	 (97)	197
		$t-C_4H_9O_2CCH_2Li$, THF, -78° to 25°	CH_3I	 (72)	197

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TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

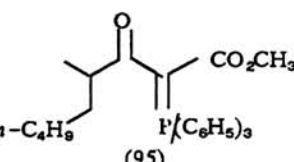
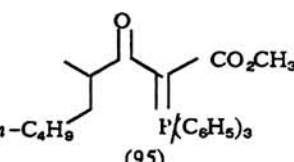
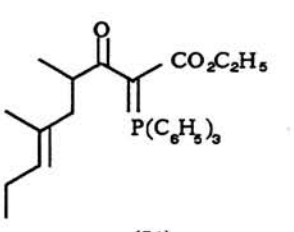
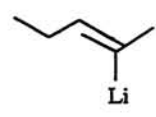
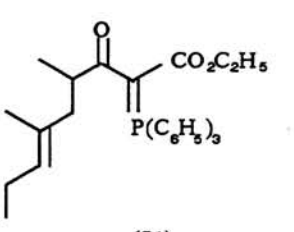
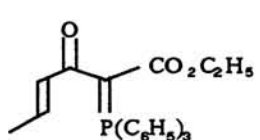
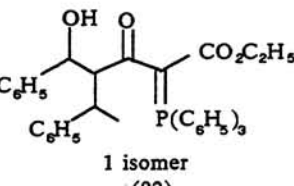
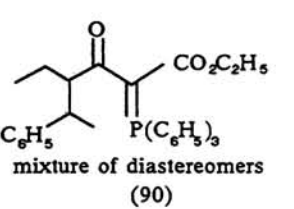
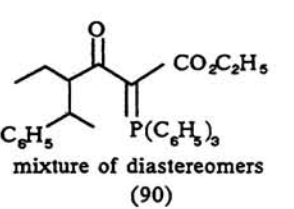
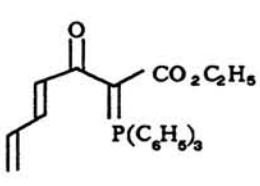
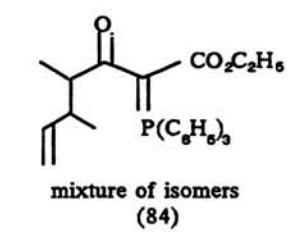
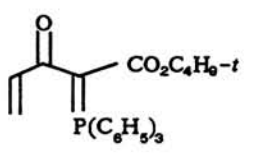
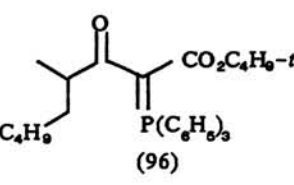
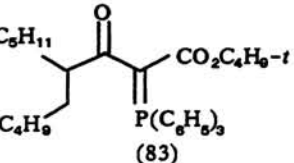
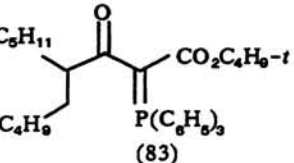
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
		$n\text{-C}_4\text{H}_9\text{Li}$	CH_3I	 (95)	198
			CH_3I	 (71)	198
26		$\text{C}_6\text{H}_5\text{Li}$, THF, -78° to 25°	$\text{C}_6\text{H}_5\text{CHO}$	 1 isomer (92)	197
		$\text{C}_6\text{H}_5\text{Li}$	$\text{C}_2\text{H}_5\text{I}$	 mixture of diastereomers (90)	198
27 ^a		CH_3Li , THF, -78° to 25°	CH_3I	 mixture of isomers (84)	197
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, -78°	CH_3I	 (96)	199
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, -78°	$n\text{-C}_6\text{H}_{11}\text{I}$, rt	 (83)	199

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)


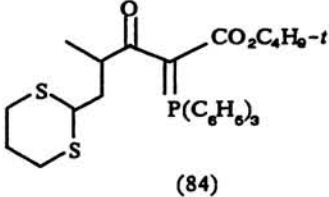
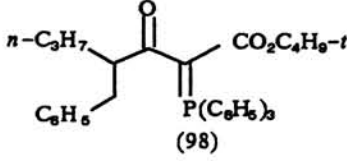
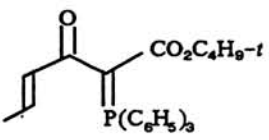
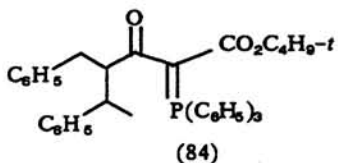
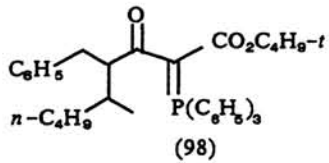
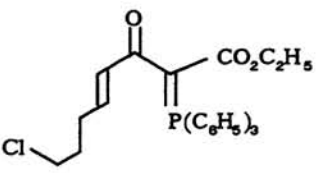
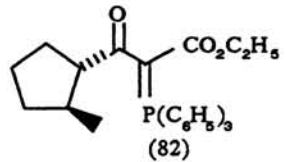
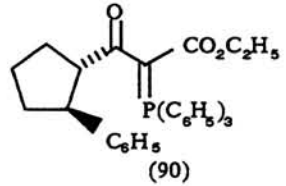
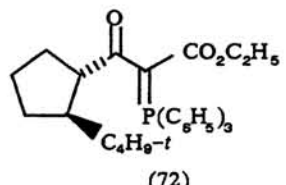
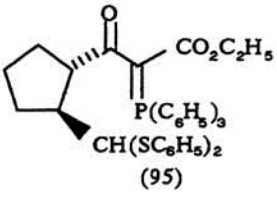
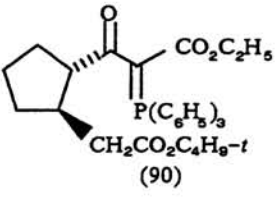
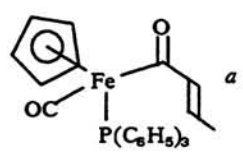
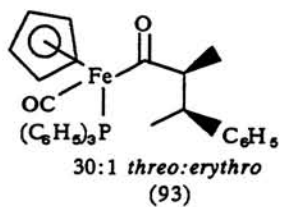
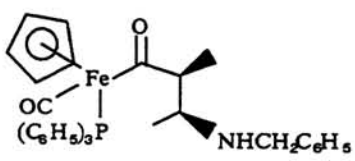
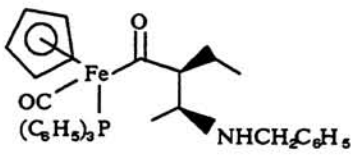
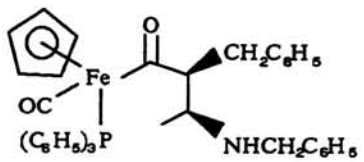

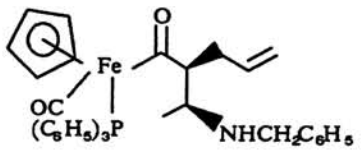
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
332		 Li, THF, -78°	CH ₃ I	 (84)	199
		C ₆ H ₅ Li, THF, -78°	<i>n</i> -C ₃ H ₇ I	 (98)	199
28 ^a		C ₆ H ₅ Li, THF, -78°	C ₆ H ₅ CH ₂ Br	 (84)	199
		<i>n</i> -C ₄ H ₉ Li, -78°, THF	C ₆ H ₅ CH ₂ Br	 (98)	199
		CH ₃ Li, THF, -78°	Intramolecular	 (82)	353
333		C ₆ H ₅ Li, THF, -78°	Intramolecular	 (90)	353
		<i>t</i> -C ₄ H ₉ Li, THF, -78°	Intramolecular	 (72)	353

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
		$(\text{C}_6\text{H}_5\text{S})_2\text{CHLi}$, THF, -78°	Intramolecular	 (95)	353
		$t\text{-C}_4\text{H}_9\text{O}_2\text{CCH}_2\text{Li}$, THF, -78°	Intramolecular	 (90)	353
		$\text{C}_6\text{H}_5\text{Li}$	CH_3I	 30:1 <i>threo:erythro</i> (93)	200 354
		$\text{C}_6\text{H}_5\text{CH}_2\text{NHLi}$	CH_3I	 24:1 <i>threo:erythro</i> (95)	200 354
		$\text{C}_6\text{H}_5\text{CH}_2\text{NHLi}$	$\text{C}_2\text{H}_5\text{I}$	 20:1 <i>threo:erythro</i> (99)	200 354
		$\text{C}_6\text{H}_5\text{CH}_2\text{NHLi}$	$\text{C}_2\text{H}_5\text{CH}_2\text{Br}$	 15:1 <i>threo:erythro</i> (99)	200 354
		$\text{C}_6\text{H}_5\text{CH}_2\text{NHLi}$		 30:1 <i>threo:erythro</i> (92)	200 354

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TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

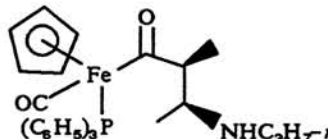
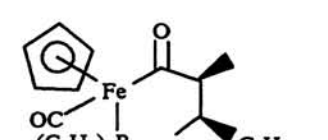
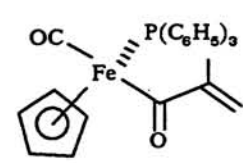
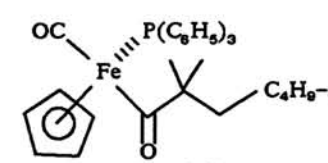
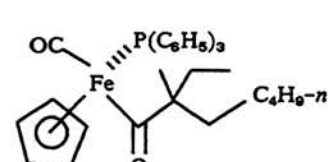
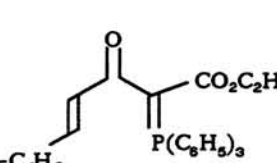
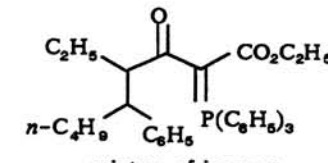
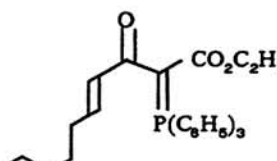
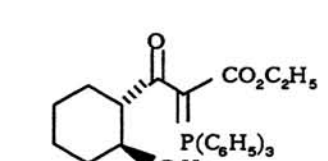
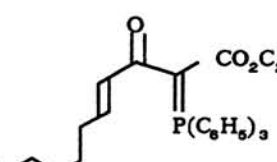
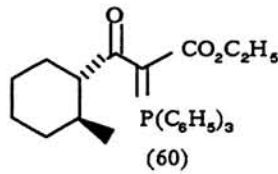
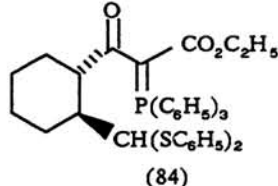
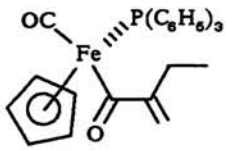
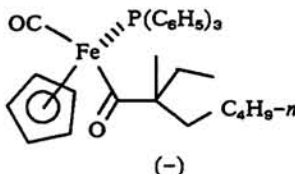
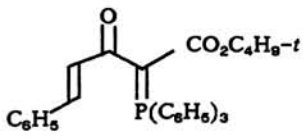
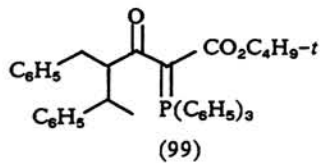
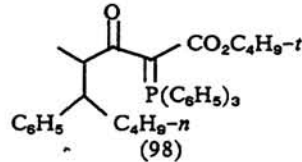
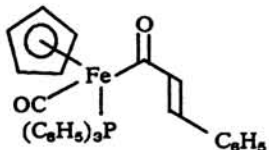
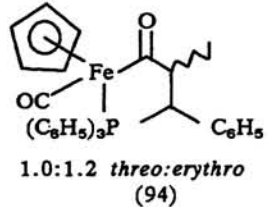
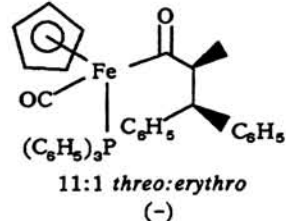
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
336		$n\text{-C}_3\text{H}_7\text{NHLi}$	CH_3I	 10:1 <i>threo:erythro</i> (53)	354
		$n\text{-C}_4\text{H}_9\text{Li}$	CH_3I	 (-)	223
		$n\text{-C}_4\text{H}_9\text{Li}$, THF	CH_3I	 (75)	355
		$n\text{-C}_4\text{H}_9\text{Li}$, THF	$\text{C}_2\text{H}_5\text{I}$	 (82)	355
	 29 ^a $n\text{-C}_4\text{H}_9$	$\text{C}_6\text{H}_5\text{Li}$, THF, -78° to 25°	$\text{C}_2\text{H}_5\text{I}$	 mixture of isomers (78)	197
337		$\text{C}_6\text{H}_5\text{Li}$, THF, -78°	Intramolecular	 (79)	353
		$\text{C}_6\text{H}_5\text{Li}$, THF, -78°	Intramolecular	" (70)	353

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
		CH_3Li , THF, -78°	Intramolecular		353
		$(\text{C}_6\text{H}_5\text{S})_2\text{CHLi}$, THF, -78°	Intramolecular		353
30 ^a		$n\text{-C}_4\text{H}_9\text{Li}$, THF	CH_3I		355
33		CH_3Li , THF, -78°	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$		199
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, -78°	CH_3I		199
33		CH_3Li	CH_3I		354
		$\text{C}_6\text{H}_5\text{Li}$	CH_3I		354

^a See addendum to Table IA for additional entries.

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
5 ^a		$(\text{CH}_3)_2\text{CuLi}$, $(i\text{-C}_3\text{H}_7)_2\text{O}$	CH_3COCl		(47.1) 272
		$\text{CH}_3\text{SCH}=\text{CHCH}_2\text{Li}$, THF, HMPA, -78°	$(\text{CH}_3)_3\text{SiC}\equiv\text{CCH}_2\text{I}$		(75) 151
			CH_3I , THF, HMPA		(65) 169
			$n\text{-C}_7\text{H}_{16}\text{I}$, THF, HMPA		(-) 169
			$n\text{-C}_8\text{H}_{17}\text{I}$, THF, HMPA		(-) 169
		$\text{Li}(n\text{-C}_9\text{H}_7\text{C}\equiv\text{C})\text{Cu}$ HMPA, -78°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, $\text{NH}_3(1)$		(24) 280
		$\text{Li}(n\text{-C}_9\text{H}_7\text{C}\equiv\text{C})\text{Cu}$ -78°			(16) 356

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

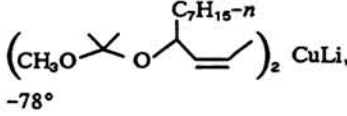
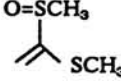
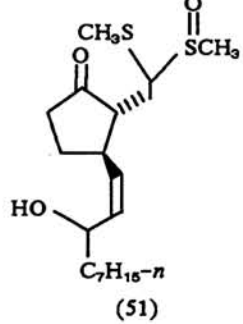
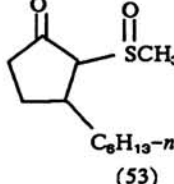
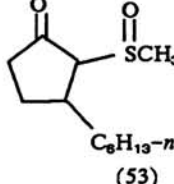
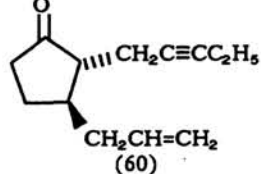
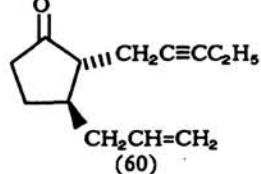
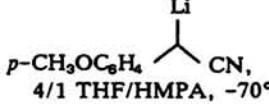
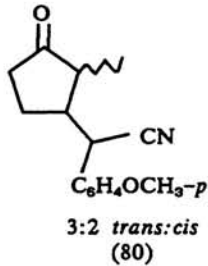
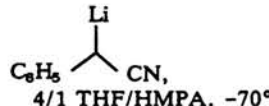
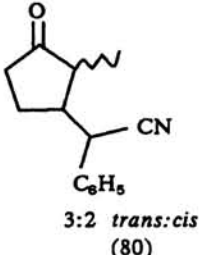
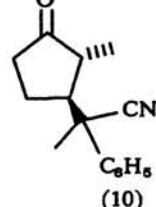
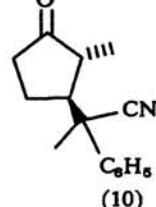
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
342		$(\text{CH}_3\text{O})_2\text{C}(\text{CH}_3)\text{O}(\text{C}_7\text{H}_{15-n})_2 \text{CuLi}, -78^\circ$	1) $\text{O}=\text{SCH}_3$  2) H_3O^+	 (51)	337
		$n\text{-C}_8\text{H}_{13}\text{MgBr}, 2 \text{ mol } \% \text{ CuI}, -30^\circ$	CH_3SOCl	 (53)	357
		$(\text{CH}_2=\text{CHCH}_2)_2\text{CuLi}, \text{THF}, -78^\circ$	$\text{C}_2\text{H}_5\text{C}\equiv\text{CCH}_2\text{I}, \text{TMEDA/HMPA}$	 (60)	358
		$p\text{-CH}_3\text{OC}_6\text{H}_4\text{LiCN}, 4/1 \text{ THF/HMPA}, -70^\circ$	CH_3I	 3:2 <i>trans:cis</i> (80)	183
343		$\text{C}_6\text{H}_5\text{LiCN}, 4/1 \text{ THF/HMPA}, -70^\circ$	CH_3I	 3:2 <i>trans:cis</i> (80)	183
				 (10)	

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
344		C_6H_5 , Li, CN, 4/1 THF/HMPA, -70°	CH_3I	 1:1 <i>trans:cis</i> (95)	183
		$(\text{CH}_3)_2\text{AlSC}_6\text{H}_5$, CH_2Cl_2 , -78°	H_2CO , THF	 (56)	204
		$(\text{CH}_3)_2\text{AlSC}_6\text{H}_5$, CH_2Cl_2 , -78°	$n\text{-C}_8\text{H}_{17}\text{CHO}$, THF	 (76)	204
		$(n\text{-C}_3\text{H}_7\text{C}\equiv\text{C})\text{CuLi}$, $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$, -78°	$(\text{C}_6\text{H}_5)_2\text{S}_2$, THF/HMPA	 (38)	119
		$\text{C}_6\text{H}_5\text{SCuLi}$, OTHP , $\text{C}_5\text{H}_{11}\text{-}n$	$\text{C}_6\text{H}_5\text{SCL}$, THF/HMPA	 (24)	119
		$n\text{-C}_5\text{H}_{11}$, Li, NC, $\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$, THF/HMPA, -78°	$\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_3\text{C}\equiv\text{CCH}_2\text{I}$	 NC, $\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$ (≤ 20)	186
345		Li, $\text{CH}_3\text{O}_2\text{CCHSi}(\text{C}_6\text{H}_5)_2\text{CH}_3$, HMPA/THF, 0°	(<i>Z</i>)- $\text{C}_2\text{H}_5\text{CH}=\text{CHCH}_2\text{Br}$, inverse addition, THF/HMPA	 CO_2CH_3 , $\text{Si}(\text{C}_6\text{H}_5)_2\text{CH}_3$ (56)	318

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

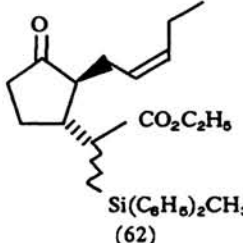
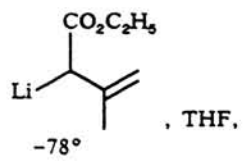
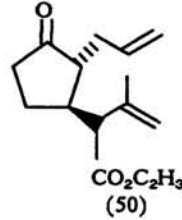
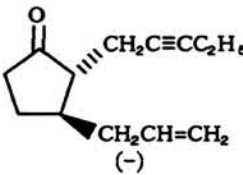
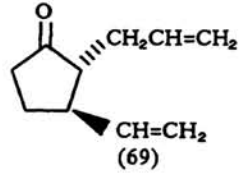
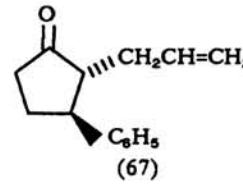
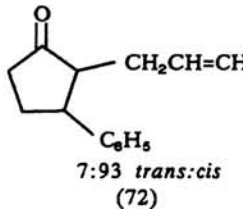
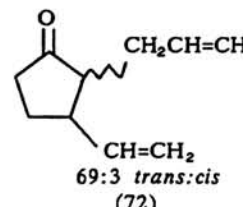
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$\begin{array}{c} \text{Li} \\ \\ \text{C}_2\text{H}_5\text{O}_2\text{CCHSi}(\text{C}_6\text{H}_5)_2\text{CH}_3 \\ \text{HMPA/THF, } 0^\circ \end{array}$	(Z)-C ₂ H ₅ CH=CHCH ₂ Br, inverse addition, THF/HMPA	 Si(C ₆ H ₅) ₂ CH ₃ (62)	318
		 -78° , THF,	CH ₂ =CHCH ₂ Br, HMPA/THF	 CO ₂ C ₂ H ₅ (50)	127
		(CH ₂ =CHCH ₂) ₂ CuLi	C ₂ H ₅ C≡CCH ₂ I	 CH ₂ C≡CC ₂ H ₅ CH ₂ CH=CH ₂ (-)	316
		CH ₃ Cu(CH=CH ₂)Li, THF	CH ₂ =CHCH ₂ Br	 CH ₂ CH=CH ₂ CH=CH ₂ (69)	316
		(C ₆ H ₅) ₂ CuLi, THF	CH ₂ =CHCH ₂ Br	 CH ₂ CH=CH ₂ C ₆ H ₅ (67)	316
		(C ₆ H ₅) ₂ CuLi, THF	CH ₂ =CHCH ₂ Br	 CH ₂ CH=CH ₂ C ₆ H ₅ 7:93 trans:cis (72)	67
		CH ₂ =CHCu(CH ₃)Li, THF, -78°	CH ₂ =CHCH ₂ Br	 CH ₂ CH=CH ₂ CH=CH ₂ 69:3 trans:cis (72)	118

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

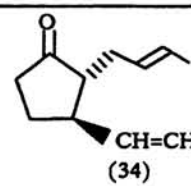
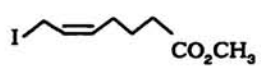
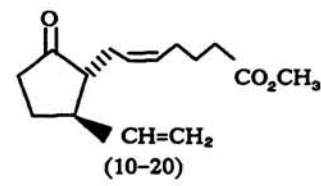
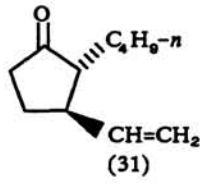
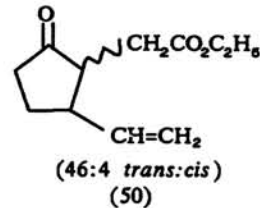
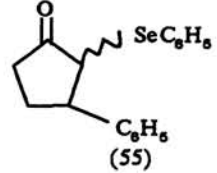
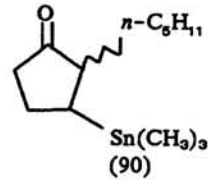
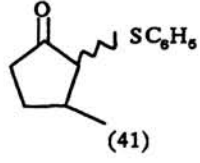
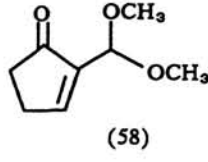
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
348		$\text{CH}_2=\text{CHCu}(\text{CH}_3)\text{Li}$, THF, -78°	$(E)\text{-CH}_3\text{CH}=\text{CHCH}_2\text{I}$	 (34)	118
		$\text{CH}_2=\text{CHCu}(\text{CH}_3)\text{Li}$, THF, -78°		 (10-20)	118
		$\text{CH}_2=\text{CHCu}(\text{CH}_3)\text{Li}$, THF, -78°	$n\text{-C}_4\text{H}_9\text{I}$	 (31)	118
		$\text{CH}_2=\text{CHCu}(\text{CH}_3)\text{Li}$, THF, -78°	$\text{C}_2\text{H}_5\text{O}_2\text{CCH}_2\text{Br}$	 (46:4 <i>trans:cis</i>) (50)	118
		$(\text{C}_6\text{H}_5)_2\text{CuLi}$	$\text{C}_6\text{H}_5\text{SeBr}$	 (55)	347
349		$(\text{CH}_3)_3\text{SnLi}$, 1:2 THF/ NH_3 , -70°	$n\text{-C}_6\text{H}_{11}\text{I}$	 (90)	206
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{C}_6\text{H}_5\text{SCl}$	 (41)	182
		$(\text{CH}_3)_3\text{SiSeC}_6\text{H}_5$, cat. $(\text{CH}_3)_3\text{SiO}_2\text{CCF}_3$, CH_2Cl_2 , -78°	$\text{HC}(\text{OCH}_3)_3$	 (58)	205

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

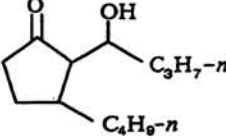
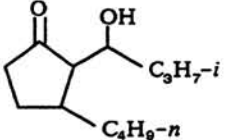
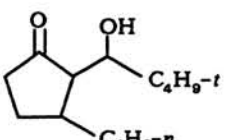
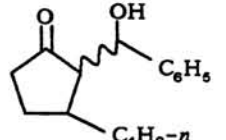
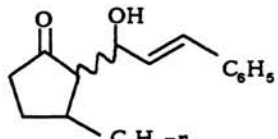
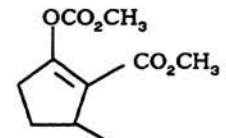
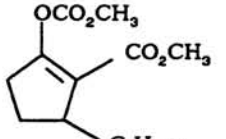
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$n\text{-C}_4\text{H}_9\text{Cu}$, 2 eq ($n\text{-C}_4\text{H}_9$) ₃ P, -78°	$n\text{-C}_3\text{H}_7\text{CHO}$	 1 isomer (98)	14
		$n\text{-C}_4\text{H}_9\text{Cu}$, 2 eq ($n\text{-C}_4\text{H}_9$) ₃ P, -78°	$i\text{-C}_3\text{H}_7\text{CHO}$	 1 isomer (93)	14
		$n\text{-C}_4\text{H}_9\text{Cu}$, 2 eq ($n\text{-C}_4\text{H}_9$) ₃ P, -78°	$t\text{-C}_4\text{H}_9\text{CHO}$	 1 isomer (71)	14
		$n\text{-C}_4\text{H}_9\text{Cu}$, 2 eq ($n\text{-C}_4\text{H}_9$) ₃ P, -78°	$\text{C}_6\text{H}_5\text{CHO}$	 mixture of isomers (91)	14
		$n\text{-C}_4\text{H}_9\text{Cu}$, 2 eq ($n\text{-C}_4\text{H}_9$) ₃ P, -78°	$(E)\text{-C}_6\text{H}_5\text{CH=CHCHO}$	 mixture of isomers (94)	14
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{CH}_3\text{O}_2\text{CCl}$	 (56)	273
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, -30° to -10°	$\text{CH}_3\text{O}_2\text{CCl}$	 (71)	273

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

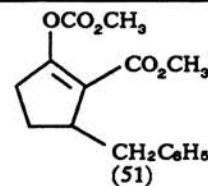
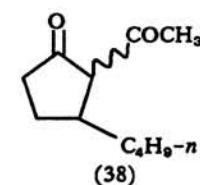
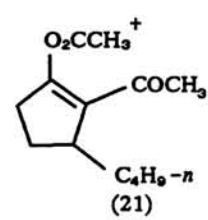
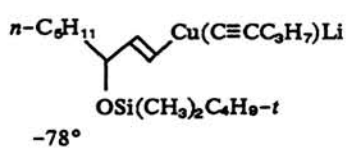
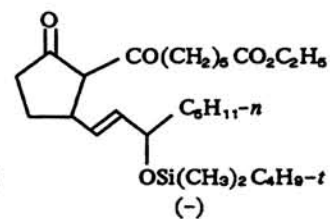
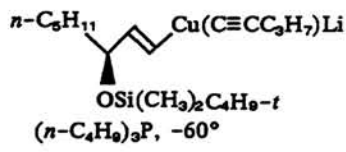
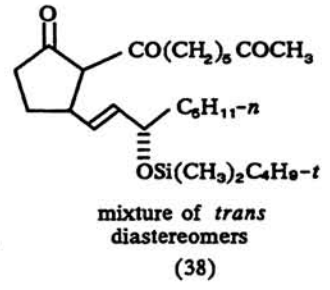
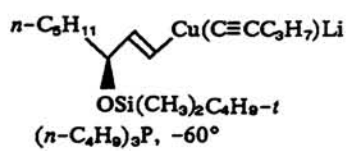
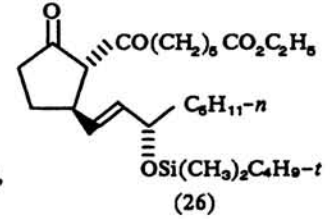
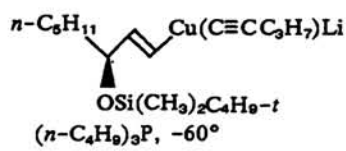
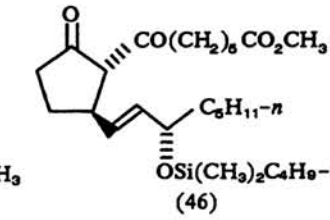
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{CuLi}$, -25° to -10°	$\text{CH}_3\text{O}_2\text{CCl}$	 (51)	273
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, $(n\text{-C}_4\text{H}_9)_3\text{P}$, -78°	CH_3COCl , HMPA	 (38)	284
				 (21)	112
		$n\text{-C}_6\text{H}_{11}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ -78°	$\text{C}_2\text{H}_5\text{O}_2\text{C}(\text{CH}_2)_6\text{COCl}$ THF/ $(\text{C}_2\text{H}_5)_2\text{O}$		284
		$n\text{-C}_6\text{H}_{11}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ $(n\text{-C}_4\text{H}_9)_3\text{P}$, -60°	$\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_6\text{COCl}$, HMPA/THF	 mixture of <i>trans</i> diastereomers (38)	112
		$n\text{-C}_6\text{H}_{11}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ $(n\text{-C}_4\text{H}_9)_3\text{P}$, -60°	$\text{C}_2\text{H}_5\text{O}_2\text{C}(\text{CH}_2)_6\text{COCl}$, HMPA/THF	 (26)	112
		$n\text{-C}_6\text{H}_{11}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ $(n\text{-C}_4\text{H}_9)_3\text{P}$, -60°	$\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_6\text{COSCH}_3$	 (46)	112

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
354	 $n\text{-C}_5\text{H}_{11}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ $(n\text{-C}_4\text{H}_9)_3\text{P}, -60^\circ$	$\text{Cu}(\text{C}\equiv\text{CC}_3\text{H}_7)\text{Li}$	 $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_5\text{CO-}$	 $\text{CO}(\text{CH}_2)_5\text{CO}_2\text{CH}_3$ $\text{C}_5\text{H}_{11}\text{-}n$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ (40)	112
	 $n\text{-C}_5\text{H}_{11}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ $(n\text{-C}_4\text{H}_9)_3\text{P}, -60^\circ$	$\text{Cu}(\text{C}\equiv\text{CC}_3\text{H}_7)\text{Li}$	 $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_5\text{COS-}$	" (25)	112
	 $n\text{-C}_5\text{H}_{11}$ OTHP $(n\text{-C}_4\text{H}_9)_3\text{P}$	$\text{Cu}(\text{C}\equiv\text{CC}_3\text{H}_7)\text{Li}$	$\text{CH}_3\text{O}_2\text{CCl}, \text{THF/HMPA}$	 CO_2CH_3 $\text{C}_5\text{H}_{11}\text{-}n$ OTHP (29)	268
				 OCO_2CH_3 CO_2CH_3 $\text{C}_5\text{H}_{11}\text{-}n$ OTHP (21)	
355	 $n\text{-C}_5\text{H}_{11}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$	$\text{Cu}(\text{C}\equiv\text{CC}_3\text{H}_7)\text{Li}$	$\text{CH}_3\text{O}_2\text{CCl}, \text{THF/HMPA}$	 CO_2CH_3 $\text{C}_5\text{H}_{11}\text{-}n$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ (55)	268
				 OCO_2CH_3 CO_2CH_3 $\text{C}_5\text{H}_{11}\text{-}n$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ (15)	
	 $\text{Si}(\text{CH}_3)_3$ $\text{TiCl}_4, \text{CH}_2\text{Cl}_2, -20^\circ$	Intramolecular		 $\text{Si}(\text{CH}_3)_3$ (48)	214

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

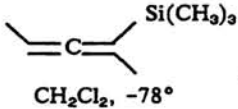
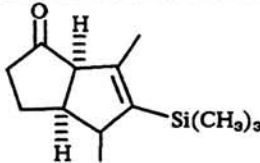
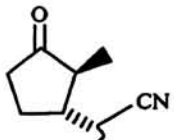
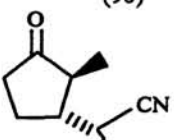
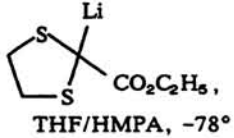
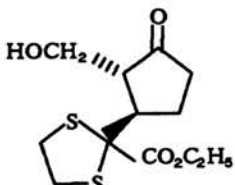
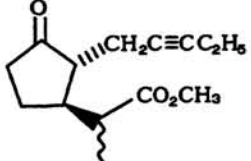
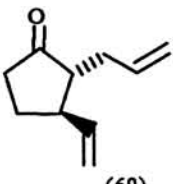
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		TiCl_4 , CH_2Cl_2 , -78°	Intramolecular	 75:25 $\beta:\alpha$ (68)	214
		$p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}(\text{CN})\text{Li}$, DME, -50°	CH_3I	 3:2 mixture of stereoisomers (90)	185
		$\text{C}_6\text{H}_5\text{CH}(\text{CN})\text{Li}$, DME, -50°	CH_3I	 3:2 mixture of stereoisomers (60)	185
		THF/HMPA, -78°	CH_2O , -78°	 (62)	222
		$(\text{CH}_3)_3\text{SiCH}=\text{C}(\text{OCH}_3)\text{Li}$, THF/HMPA, $(n\text{-C}_4\text{H}_9)_3\text{SnCl}$, -78°	$\text{BrCH}_2\text{C}\equiv\text{CC}_2\text{H}_5$	 3:1 mixture of diastereomers (54)	13
		$(\text{CH}_2=\text{CH})\text{Cu}(\text{CH}_3)\text{Li}$, -78°	$\text{CH}_2=\text{CHCH}_2\text{Br}$	 (69)	108

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.	
Section B: Cyclic Substrates						
		THF	1) $n\text{-C}_3\text{H}_7\text{COCN}$ 2) H_3O^+		299	
		THF	1) CH_3COCN 2) H_3O^+		299	
		THF	1) CH_3COCN 2) H_3O^+		299	
		$\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ $-78^\circ, \text{HMPA}$	$\text{CH}_2=\text{C}(\text{OCH}_3)\text{CH}_2\text{Br}$ $\text{NH}_3(l)$		344	
	$(\text{CH}_3)_2\text{C}=\text{CHCO}_2\text{C}_2\text{H}_5$	LDA, THF, -78°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, THF, HMPA		127	
	$(\text{CH}_2=\text{CHCH}_2)_2\text{CuLi}$, THF		$\text{ICH}_2\text{C}\equiv\text{CC}_2\text{H}_5$		358	
			THF, -50°	$\text{CH}_2=\text{CHP}(\text{C}_6\text{H}_5)_3\text{Br}^-$, DMF/THF		263

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
6		$(\text{CH}_2=\text{CCH}_3)_2\text{CuLi}$, 0°	1) $(\text{CH}_3)_3\text{Si}-\text{C}(\text{O})=\text{CH}_2$ 2) 2% KOH/CH ₃ OH, reflux	 (50-70)	291
		$(\text{CH}_2=\text{CH})_2\text{CuLi}$, 0°	1) $(\text{CH}_3)_3\text{Si}-\text{C}(\text{O})=\text{CH}_2$ 2) 2% KOH/CH ₃ OH, reflux	 (50-70)	291
		$(\text{CH}_3)_2\text{CuLi}$, 0°	1) $(\text{CH}_3)_3\text{Si}-\text{C}(\text{O})=\text{CH}_2$ 2) 2% KOH/CH ₃ OH, reflux	 (57)	291
		$\text{Cu}(\text{C}\equiv\text{CC}_3\text{H}_7)\text{Li}$ -78° to -20°	1) $(\text{CH}_3)_3\text{Si}-\text{C}(\text{O})=\text{CH}_2$ 2) 2% KOH/CH ₃ OH, reflux	 $(\text{CH}_2)_4\text{CH}(\text{OCH}_3)_2$ (80-85)	310
		$(\text{CH}_2=\text{CH})_2\text{CuMgBr}$, -70° , THF	$\text{C}_2\text{H}_5\text{O}_2\text{CCH}_2\text{Br}$, HMPA	 3:1.1 <i>trans:cis</i> (81)	290
		$\text{CH}_2=\text{CHMgBr}$, 3 mol % CuI, THF, DMS, -78°	<i>t</i> - $\text{C}_4\text{H}_9\text{O}_2\text{CCH}_2\text{Br}$, HMPA	 $\text{CH}_2\text{CO}_2\text{C}_4\text{H}_9-t$ $\text{CH}=\text{CH}_2$ >96% <i>trans</i> (-)	359
		$\text{Cu}(\text{C}\equiv\text{CC}_3\text{H}_7)\text{Li}$ 0°	$\text{CH}_3\text{O}_2\text{CCH}_2\text{Br}$, inverse addition, HMPA	 $\text{CH}_3\text{O}_2\text{CCH}_2$ H (≥ 57)	327

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

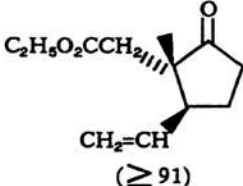
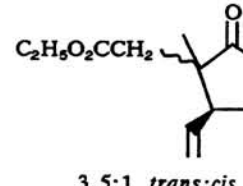
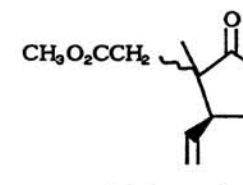
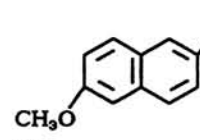
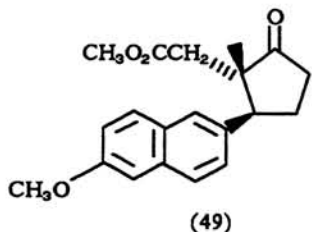
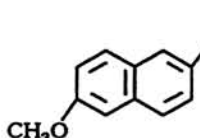
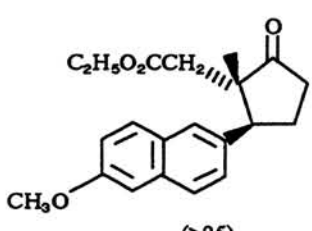
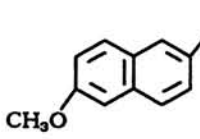
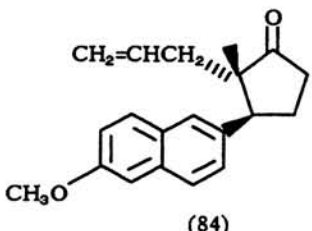
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$\text{CH}_2=\text{CHMgBr}$, cat. CuI	$\text{C}_2\text{H}_5\text{O}_2\text{CCH}_2\text{Br}$	 $\text{C}_2\text{H}_5\text{O}_2\text{CCH}_2$ $\text{CH}_2=\text{CH}$ (≥ 91)	360
		$\text{CH}_2=\text{CHMgBr}$, 1 eq CuI , THF, -60° to -40°	$\text{C}_2\text{H}_5\text{O}_2\text{CCH}_2\text{Br}$, HMPA	 $\text{C}_2\text{H}_5\text{O}_2\text{CCH}_2$ 3.5:1 <i>trans:cis</i> (69)	88
		$(\text{CH}_2=\text{CH})\text{Cu}(\text{C}\equiv\text{CC}_4\text{H}_9-t)\text{Li}$, -70° , 9/1 $(\text{C}_2\text{H}_5)_2\text{O}/\text{THF}$	$\text{CH}_3\text{O}_2\text{CCH}_2\text{Br}$, inverse addition, HMPA	 $\text{CH}_3\text{O}_2\text{CCH}_2$ 6:1 <i>trans:cis</i> (85)	345
	 $\text{Cu}(\text{C}\equiv\text{CC}_3\text{H}_7-n)\text{Li}$ CH_3O 0°		$\text{CH}_3\text{O}_2\text{CCH}_2\text{Br}$, HMPA	 $\text{CH}_3\text{O}_2\text{CCH}_2$ CH_3O (49)	114
	 $\text{Cu}(\text{C}\equiv\text{CC}_3\text{H}_7-n)\text{MgBr}$ CH_3O THF, rt		$\text{C}_2\text{H}_5\text{O}_2\text{CCH}_2\text{I}$	 $\text{C}_2\text{H}_5\text{O}_2\text{CCH}_2$ CH_3O (>95)	114
	 $\text{Cu}(\text{C}\equiv\text{CC}_3\text{H}_7-n)\text{MgBr}$ CH_3O THF, rt		$\text{CH}_2=\text{CHCH}_2\text{Br}$	 $\text{CH}_2=\text{CHCH}_2$ CH_3O (84)	114

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

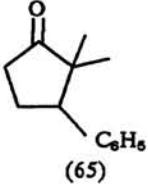
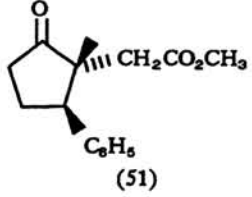
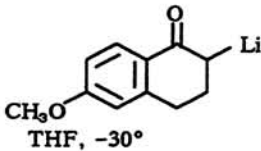
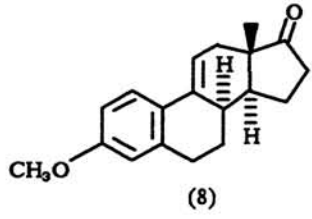
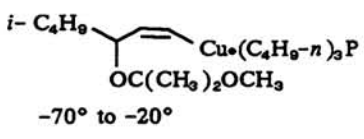
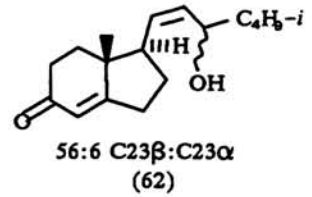
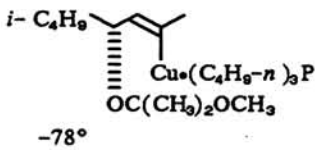
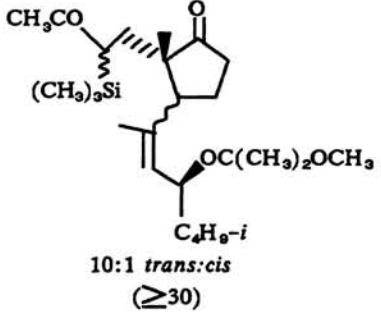
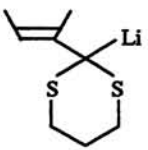
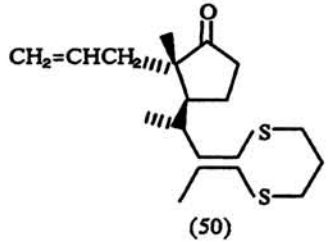
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(C_6H_5)_2CuLi, 0^\circ$	$CH_3I, HMPA, 25^\circ$	 (65)	67
		$C_6H_5Cu(C\equiv CC_2H_7)Li$	$CH_3O_2CCH_2Br, HMPA$	 (51)	67
		THF, -30°	$CH_2=CHP^+(C_6H_5)_3Br^-$, DMF/THF, rt	 (8)	263
		$Cu \cdot (C_4H_9-n)_3P$ -70° to -20°	1) $CH_2=C[Si(CH_3)_3]COCH_3$ 2) $NaOCH_3/CH_3OH, reflux$	 56:6 C23 β :C23 α (62)	361
		$Cu \cdot (C_4H_9-n)_3P$ -78°	$CH_2=C[Si(CH_3)_3]COCH_3$	 10:1 <i>trans:cis</i> (≥ 30)	328
		-78°	$CH_2=CHCH_2Br, CuI \cdot P(OCH_3)_3$	 (50)	362

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

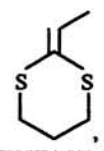
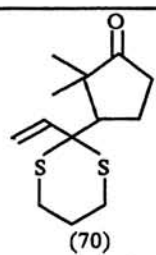
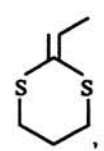
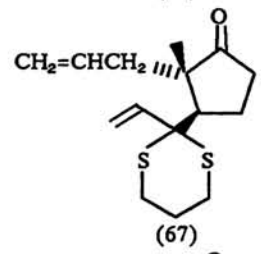
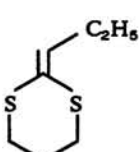
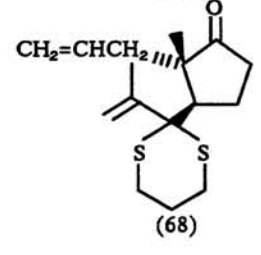
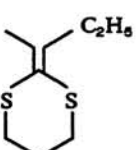
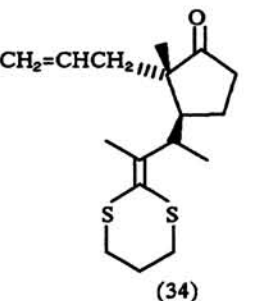
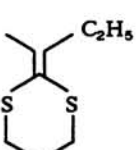
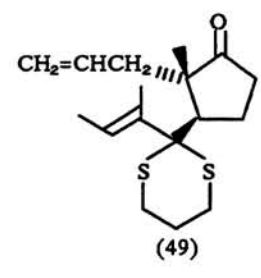
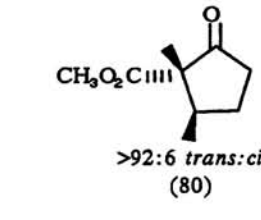
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		LDA, THF/ HMPA, -78°	CH_3I	 (70)	164
		LDA, THF/ HMPA, -78°	$\text{CH}_2=\text{CHCH}_2\text{Br}$	 (67)	164
		LDA, THF/ HMPA, -78°	$\text{CH}_2=\text{CHCH}_2\text{Br}$	 (68)	164
		LDA, THF, -78°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, $\text{CuI}\cdot\text{P}(\text{OCH}_3)_3$	 (34)	164
		LDA, THF/ HMPA, -78°	$\text{CH}_2=\text{CHCH}_2\text{Br}$	 (49)	164
		$(\text{CH}_3)_2\text{CuLi}$, 0°	1) CO_2 , -78° 2) CH_2N_2	 (80) >92:6 <i>trans:cis</i>	313

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$[t\text{-C}_4\text{H}_9\text{C}\equiv\text{CCu} \text{---} \text{OCH}_2\text{OCH}_3]^- \text{Li}^+$, THF, -45°	$\text{BrCH}_2\text{CO}_2\text{CH}_3$, HMPA, -20° , inverse addition	 (85)	338
368		, THF, 0°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, -78°	 (46)	363
		$\text{CH}_2=\text{CH} \text{---} \text{Li} \text{---} \text{SC}_6\text{H}_5$, THF, HMPA, -78°	$(E)\text{-C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{Br}$	 (53)	150
		$[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{CuLi}$, THF, -23°	CH_3I , HMPA	 (95)	63
		$[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{CuLi}$, THF, -23°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, HMPA	 (54)	63
369		$(\text{C}_6\text{H}_5)_2\text{CuLi}$, 0°	CH_3I , HMPA	 (65)	316
		$(\text{CH}_3)_3\text{Al}$, 3 mol % $\text{Ni}^{+2}(\text{ACAC})_2$, 0°		 (-)	207

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

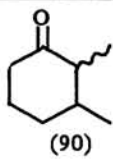
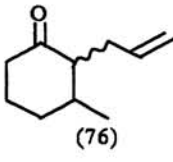
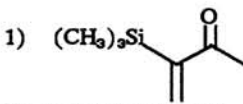
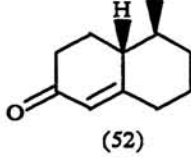
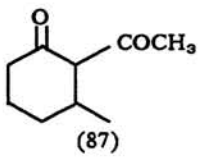
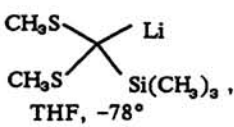
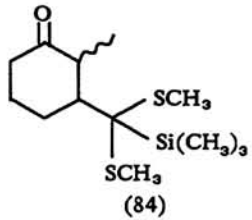
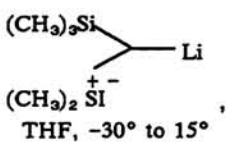
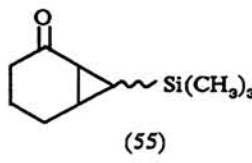
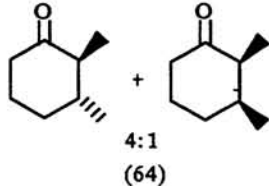
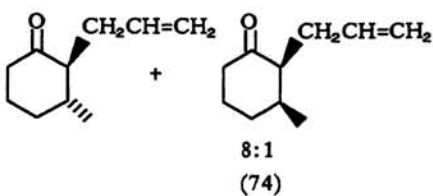
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(\text{CH}_3)_2\text{CuLi}, 0^\circ$	$\text{CH}_3\text{I}, 1/1 \text{ THF/HMPA}$	 (90)	232
		$(\text{CH}_3)_2\text{CuLi}, 0^\circ$	$\text{CH}_2=\text{CHCH}_2\text{I}, 1/1 \text{ THF/HMPA}$	 (76)	232
		$(\text{CH}_3)_2\text{CuLi}, 0^\circ$	1)  2) 2% KOH/ CH_3OH , reflux	 (52)	291
		$(\text{CH}_3)_2\text{CuLi}, (i\text{-C}_3\text{H}_7)_2\text{O}$	CH_3COCl	 (87)	272
		 THF, -78°	$\text{CH}_3\text{I}, \text{HMPA/THF}$	 (84)	169
		 THF, -30° to 15°	Intramolecular	 (55)	157
		$(\text{CH}_3)_2\text{CuLi}, 0^\circ$	$\text{CH}_3\text{I}, \text{DME}$	 4:1 (64)	221
		$(\text{CH}_3)_2\text{CuLi}, 0^\circ$	$\text{CH}_2=\text{CHCH}_2\text{Br}$	 8:1 (74)	221

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(\text{CH}_2=\text{CH})_2\text{CuLi}$, 0°	CH_3I , DME	 3:1 (48)	221
		$n\text{-C}_4\text{H}_9\text{MgBr}$, 2 mol % CuCl , -30°	 CH_3SCl	 $\text{C}_4\text{H}_9\text{-}n$ (76)	357
		$(\text{CH}_3)_2\text{CuLi}$, 0°	ZnCl_2 , CH_3CHO	 <i>erythro</i> (97)	234 220
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{C}_2\text{H}_5\text{O}_2\text{CH}$	 (44)	220
		 $p\text{-CH}_3\text{OC}_6\text{H}_4$ 4/1 THF/HMPA, -70°	CH_3I	 $\text{C}_6\text{H}_4\text{OCH}_3\text{-}p$ 1:1 mixture (65)	183
				 $\text{C}_6\text{H}_4\text{OCH}_3\text{-}p$ (20)	

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

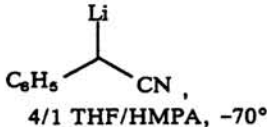
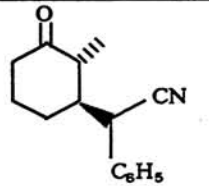
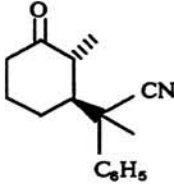

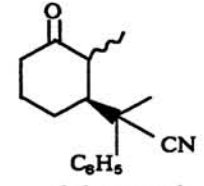
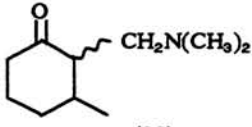
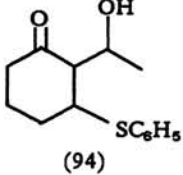
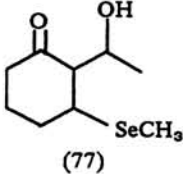
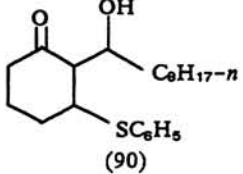
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		 C_6H_5 CN , 4/1 THF/HMPA, -70°	CH_3I	 $>95:5$ <i>trans:cis</i> (45) +  (30)	183
		 C_6H_5 CN , 4/1 THF/HMPA, -70°	CH_3I	 $1:1$ <i>trans:cis</i> (95)	183
		$(\text{CH}_3)_2\text{CuLi}$, -78°	$(\text{CH}_3)_2\text{N}^+\text{=CH}_2\text{O}_2\text{CCF}_3$	 (80)	364
		$(\text{CH}_3)_2\text{AlSC}_6\text{H}_5$, CH_2Cl_2 , -78°	CH_3CHO , THF	 (94)	204
		$(\text{CH}_3)_2\text{AlSeCH}_3$, CH_2Cl_2 , -78°	CH_3CHO , THF	 (77)	204
		$(\text{CH}_3)_2\text{AlSC}_6\text{H}_5$, CH_2Cl_2 , -78°	$n\text{-C}_8\text{H}_{17}\text{CHO}$, THF	 (90)	204

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

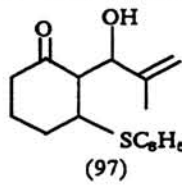
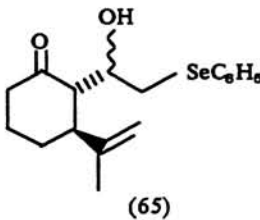
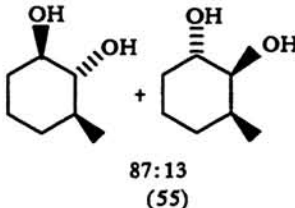
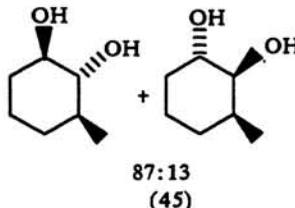
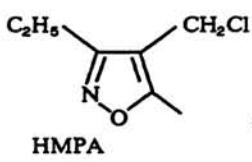
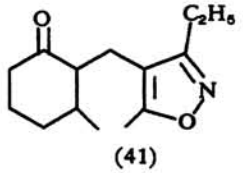
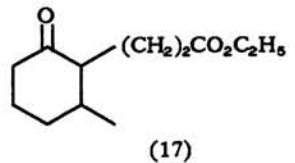
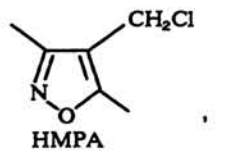
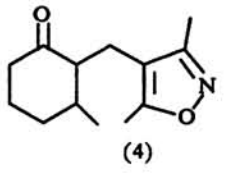
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(\text{CH}_3)_2\text{AlSC}_6\text{H}_5$, CH_2Cl_2 , -78°	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}$, THF	 (97)	204
		$[\text{CH}_2=\text{C}(\text{CH}_3)]_2\text{CuLi}$, DMS, -25°	$\text{C}_6\text{H}_5\text{SeCH}_2\text{CHO}$, -78°	 (65)	104
		$(\text{CH}_3)_2\text{CuLi}$, -10°	1) $\text{BH}_3 \cdot \text{THF}$ 2) alkaline H_2O_2	 87:13 (55)	346
		CH_3MgBr , cat. CuCl , -10°	1) $\text{BH}_3 \cdot \text{THF}$ 2) alkaline H_2O_2	 87:13 (45)	346
		CH_3MgBr , 2.8 mol % CuCl , 0°	 HMPA	 (41)	365
		CH_3MgI , 2.8 mol % CuCl , 0°	$\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$	 (17)	365
		CH_3MgI , 5 mol % CuCl , 0°	 HMPA	 (4)	294

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

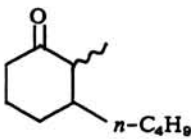
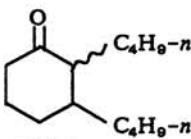
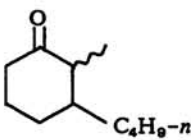
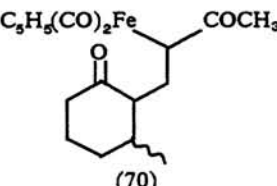
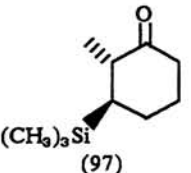
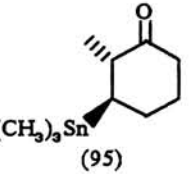
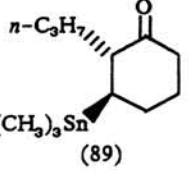
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, THF, -78°	CH_3I , HMPA	 7:1 <i>trans:cis</i> (84)	118
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, THF, -78°	$n\text{-C}_4\text{H}_9\text{I}$, HMPA	 4.5:1 <i>trans:cis</i> (50)	118
		$n\text{-C}_4\text{H}_9\text{Cu}(\text{OC}_4\text{H}_9\text{-}t)\text{Li}$, THF, -78°	CH_3I , HMPA	 35:4 <i>trans:cis</i> (39)	118
		$(\text{CH}_3)_2\text{CuLi}$, -78°	$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]^\dagger$ $\text{CH}_2=\text{CHCOCH}_3$	 (70)	366
		$(\text{CH}_3)_3\text{SiLi}$, 5/1 THF/HMPA, -78°	CH_3I	 (97)	55
		$(\text{CH}_3)_3\text{SnLi}$, THF, -78°	CH_3I	 (95)	206
		$(\text{CH}_3)_3\text{SnLi}$, 1/2 THF/ NH_3 , -70°	$n\text{-C}_3\text{H}_7\text{I}$, -33°	 (89)	206

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

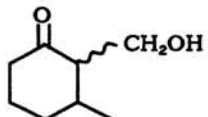
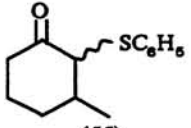
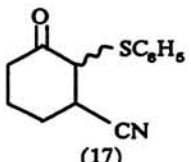
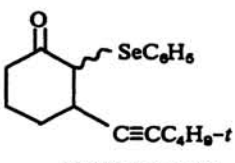
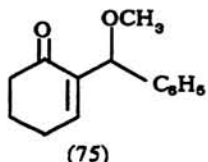
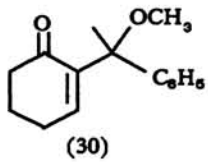
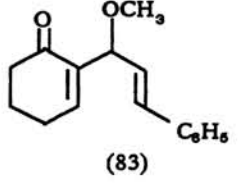
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		CH_3MgBr , 1% $\text{CuI} \cdot \text{P}(\text{C}_4\text{H}_9-n)_3$, -78°	$\text{CH}_2\text{O}(\text{g})$, -10°	 1:5 ratio of diastereomers (70)	76
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{C}_6\text{H}_5\text{SCl}$	 (55)	182
		$(\text{C}_2\text{H}_5)_2\text{AlCN}$	$\text{C}_6\text{H}_5\text{SCl}$, HMPA	 (17)	182
		$\text{CH}_3(\text{CH}_3\text{O})\text{AlC}\equiv\text{CC}_4\text{H}_9-t$ $\text{Ni}(\text{acac})_2$ $(i-\text{C}_4\text{H}_9)_2\text{AlH}$, 0°	$\text{C}_6\text{H}_5\text{SeBr}$, $(\text{C}_6\text{H}_5)_2\text{Se}_2$, -78°	 33:10 <i>trans:cis</i> (43)	209
		$(\text{CH}_3)_3\text{SiSeC}_6\text{H}_5$, cat. $(\text{CH}_3)_3\text{SiO}_2\text{CCF}_3$, CH_2Cl_2 , -78°	1) $\text{C}_6\text{H}_5\text{CH}(\text{OCH}_3)_2$ 2) [O]	 (75)	205
		$(\text{CH}_3)_3\text{SiSeC}_6\text{H}_5$, cat. $(\text{CH}_3)_3\text{SiO}_2\text{CCF}_3$, CH_2Cl_2 , -78°	1) $\text{C}_6\text{H}_5\text{CCH}_3(\text{OCH}_3)_2$ 2) [O]	 (30)	205
		$(\text{CH}_3)_3\text{SiSeC}_6\text{H}_5$, cat. $(\text{CH}_3)_3\text{SiO}_2\text{CCF}_3$, CH_2Cl_2 , -78°	1) $(E)\text{-C}_6\text{H}_5\text{CH}=\text{CHCH}(\text{OCH}_3)_2$ 2) [O]	 (83)	205

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

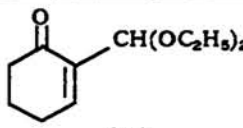
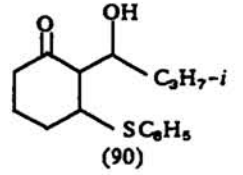
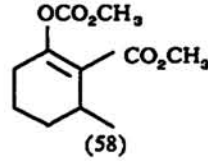
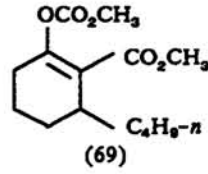
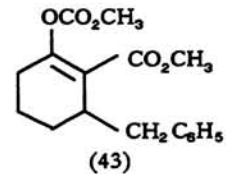
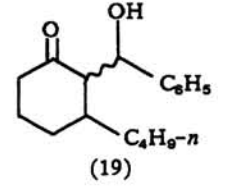
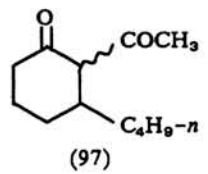
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(\text{CH}_3)_3\text{SiSeC}_6\text{H}_5$, cat. $(\text{CH}_3)_3\text{SiO}_2\text{CCF}_3$, CH_2Cl_2 , -78°	1) $\text{HC}(\text{OC}_2\text{H}_5)_3$ 2) [O]	 (76)	205
		$\text{C}_6\text{H}_5\text{SMgI}$, $(\text{C}_2\text{H}_5)_2\text{O}$ /hexane, 0°	$i\text{-C}_3\text{H}_7\text{CHO}$	 (90)	145
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{CH}_3\text{O}_2\text{CCl}$	 (58)	273
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, -30° to -10°	$\text{CH}_3\text{O}_2\text{CCl}$	 (69)	273
		$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{CuLi}$, -25° to -10°	$\text{CH}_3\text{O}_2\text{CCl}$	 (43)	273
		$n\text{-C}_4\text{H}_9\text{Cu}$, 2.2 eq $(n\text{-C}_4\text{H}_9)_3\text{P}$, -78°	$\text{C}_6\text{H}_5\text{CHO}$	 (19)	367
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, $(n\text{-C}_4\text{H}_9)_3\text{P}$, -78°	CH_3COCl , HMPA	 (97)	284 112
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, $(n\text{-C}_4\text{H}_9)_3\text{P}$, -78°	CH_3COCl	" (56)	284 112

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

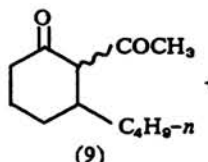
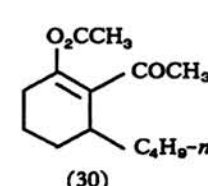
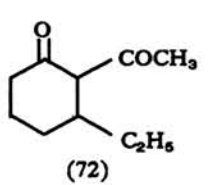
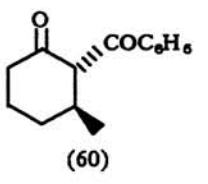
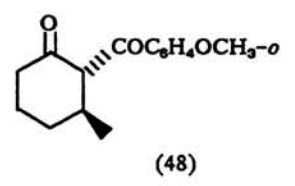
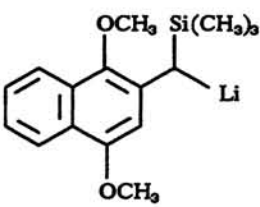
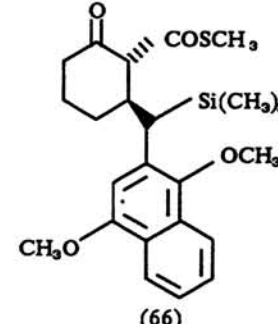
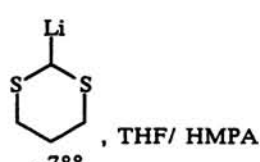
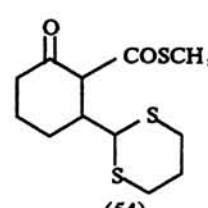
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, -78°	$(\text{CH}_3\text{CO})_2\text{O}$, HMPA	 (9)	284
				 (30)	112
		$(\text{C}_2\text{H}_5)_2\text{CuLi}$, -78°	CH_3COCl , HMPA/THF	 (72)	112
		$(\text{CH}_3)_2\text{CuLi}$, rt	$\text{C}_6\text{H}_5\text{COCl}$, HMPA	 (60)	270
		$(\text{CH}_3)_2\text{CuLi}$, rt	$o\text{-CH}_3\text{OC}_6\text{H}_4\text{COCl}$	 (48)	270
		THF, HMPA, -78°	COS , $\text{C}_6\text{H}_5\text{CH}_3$, CH_3I	 (66)	189
		THF/ HMPA, -78°	COS , CH_3I	 (54)	189

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

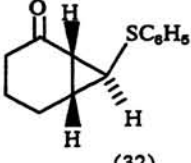
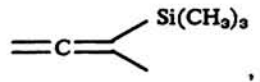
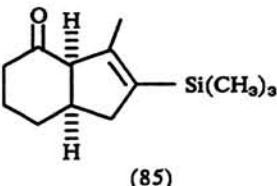
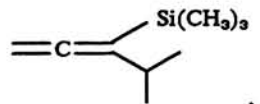
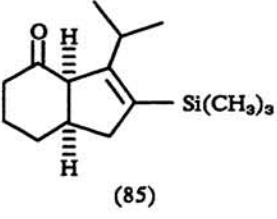
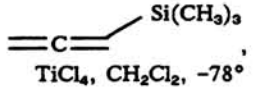
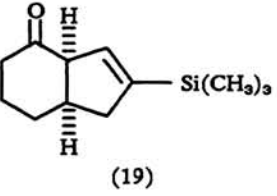
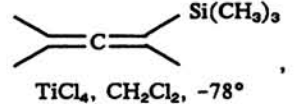
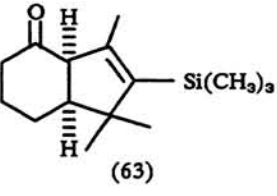
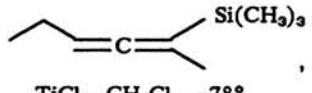
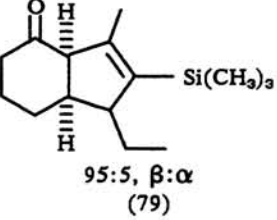
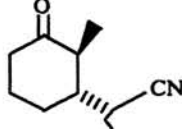
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		1) $(C_6H_5S)_3CLi$ 2) $s-C_4H_9Li$ 3) 1.0 eq CH_3OH	CH_3I , HMPA	 (32)	167
		$TiCl_4$, CH_2Cl_2 , -78°	Intramolecular	 (85)	214
		$TiCl_4$, CH_2Cl_2 , -78°	Intramolecular	 (85)	214
		$TiCl_4$, CH_2Cl_2 , -78°	Intramolecular	 (19)	214
		$TiCl_4$, CH_2Cl_2 , -78°	Intramolecular	 (63)	214
		$TiCl_4$, CH_2Cl_2 , -78°	Intramolecular	 95:5, $\beta:\alpha$ (79)	214
	$p-CH_3OC_6H_4CH(CN)Li$, DME, -50°		CH_3I	 $p-CH_3OC_6H_4$ 7:3 mixture of stereoisomers (80)	185

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

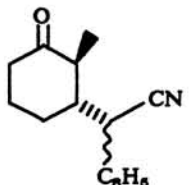
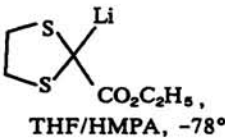
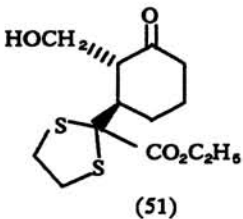
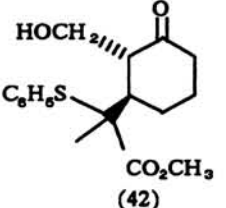
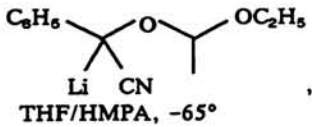
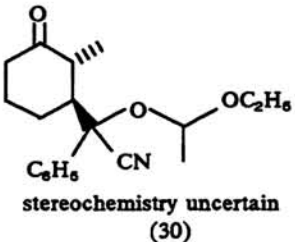
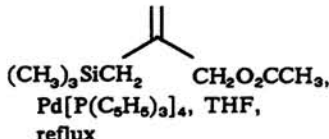
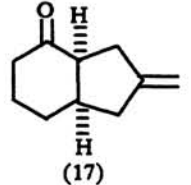
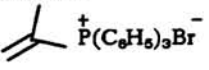


Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$\text{C}_6\text{H}_5\text{CH}(\text{CN})\text{Li}$, DME, -50°	CH_3I	 1:1 mixture of stereoisomers (80)	185
		 THF/HMPA, -78°	CH_2O	 (51)	222
		$\text{C}_6\text{H}_5\text{SC}(\text{CH}_3)\text{LiCO}_2\text{CH}_3$, THF/HMPA, -78°	CH_2O	 (42)	222
		 THF/HMPA, -65°	CH_3I	 stereochemistry uncertain (30)	187
		 $(\text{CH}_3)_3\text{SiCH}_2$ $\text{CH}_2\text{O}_2\text{CCH}_3$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF, reflux	Intramolecular	 (17)	215
		1) LDA, THF 2) 	Intramolecular	 (17)	176
		1) LDA, THF 2) $\text{CH}_2=\text{C}(\text{CH}_3)\text{P}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$, pyridine	Intramolecular	 (17)	175

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

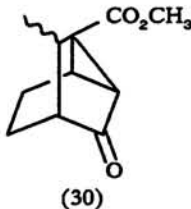
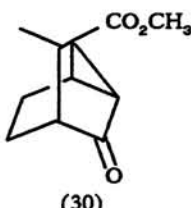
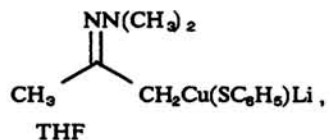
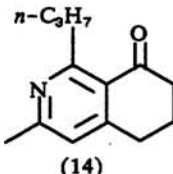
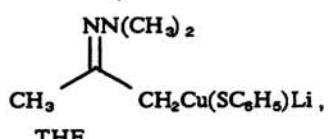
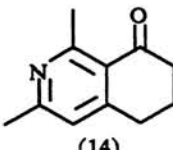
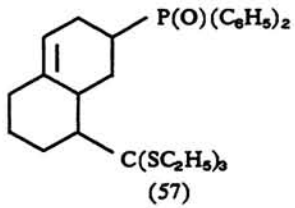
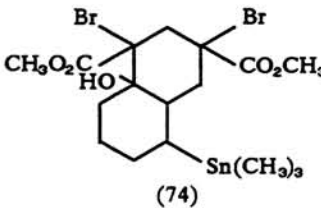
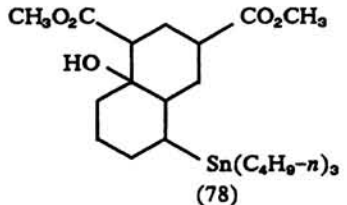
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		1) LDA, HMPA, THF, -19° 2) $\text{CH}_3\text{CH}=\text{CBrCO}_2\text{CH}_3$	Intramolecular	 (30)	368
		1) LDA 2) $\text{CH}_3\text{CH}=\text{CBrCO}_2\text{CH}_3$	Intramolecular	 (30)	369
		$\text{CH}_2\text{Cu}(\text{SC}_6\text{H}_5)\text{Li}$, THF	1) $n\text{-C}_3\text{H}_7\text{COCN}$ 2) H_3O^+	 (14)	299
		$\text{CH}_2\text{Cu}(\text{SC}_6\text{H}_5)\text{Li}$, THF	1) CH_3COCN 2) H_3O^+	 (14)	299
		$\text{LiC}(\text{SC}_2\text{H}_5)_3$	1) $\text{CH}_2=\text{CHP}^+(\text{C}_6\text{H}_5)_2\text{Br}^-$ 2 eq 2) KOH	 (57)	168
		$\text{LiSn}(\text{CH}_3)_3$	$\text{CH}_2=\text{CBrCO}_2\text{CH}_3$ 2 eq	 (74)	168
		$\text{LiSn}(\text{C}_4\text{H}_9-n)_3$	$\text{CH}_2=\text{CHCO}_2\text{CH}_3$ 2 eq	 (78)	168

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

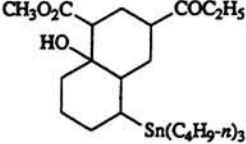

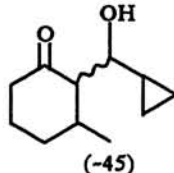

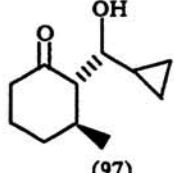
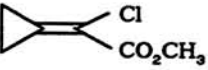

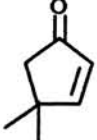
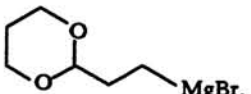
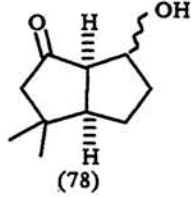
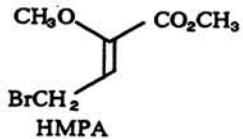
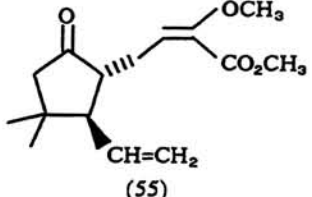
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$\text{LiSn}(\text{C}_4\text{H}_9-n)_3$	1) $\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$ 2) $\text{CH}_2=\text{CHCO}_2\text{CH}_3$	 (64)	168
		CH_3MgI , cat. CuI , 0°	 CHO	 (-45)	370
		CH_3MgI , cat. CuI , 0°	 CHO	 (97)	371
		1) LDA 2) 	Intramolecular	 (20)	372
7		 $\text{CuBr}\cdot\text{DMS}$, THF, -78°	HCl , H_2O , THF	 (78)	278
		$\text{CH}_2=\text{CHMgBr}$, $\text{CuI}\cdot(n\text{-C}_4\text{H}_9)_3\text{P}$	 HMPA	 (55)	324

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
396		$(\text{CH}_2=\text{CH})_2\text{CuLi}$, 0°	1) $(\text{CH}_3)_3\text{Si}-\text{C}(\text{O})=\text{CH}_2$ 2) 2% KOH/ CH_3OH , reflux	 (70)	291
		$(\text{CH}_3)_2\text{CuLi}$, 0°	ZnCl_2 , CH_3CHO	 (32)	234
		$(\text{CH}_3)_2\text{AlSC}_6\text{H}_5$, CH_2Cl_2 , -78°	CH_3CHO , THF	 (75)	204
		 THF/HMPA, -78°	CH_2O	 (49)	222
		$\text{C}_6\text{H}_5\text{SC}(\text{CH}_3)\text{LiCO}_2\text{CH}_3$, THF/HMPA, -78°	CH_2O	 (47)	222
		1) LDA, THF 2) $\text{CH}_2=\text{CH}^+\text{C}(\text{C}_6\text{H}_5)_3\text{Br}^-$	Intramolecular	 (10)	174 175
		$[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{CuLi}$, THF, -23°	CH_3I , HMPA	 (64)	63

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

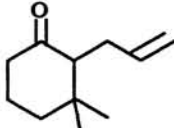
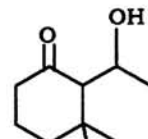
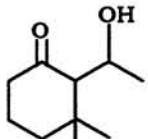
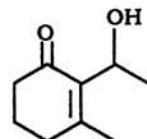
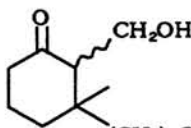
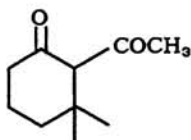
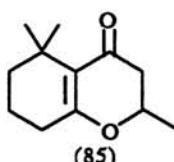
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
					
		$[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{CuLi}$, THF, -23°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, HMPA	$\text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_5$ (66)	63
		$(\text{CH}_3)_2\text{CuLi}$, 0°	ZnCl_2 , CH_3CHO	 <i>threo</i> (98)	234 220
		CH_3MgI , cat. CuI , -5°	CH_3CHO	 (75)	271
		$(\text{CH}_3)_2\text{AlSC}_6\text{H}_5$, CH_2Cl_2 , -78°	CH_3CHO , THF	 (50)	204
		$(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_2)_2\text{MgBr}$, 5 mol % $\text{CuBr}\cdot\text{DMS}$, THF, 0°	$\text{H}_2\text{CO}(\text{g})$	 $(\text{CH}_2)_2\text{CH}=\text{C}(\text{CH}_3)_2$ 1:1 <i>trans:cis</i> (90)	322
		CH_3MgI , cat. CuI , -5°	CH_3COCl	 (62)	271
		CH_3MgI , cat. CuI , -5°	$(E)\text{-CH}_3\text{CH}=\text{CHCOCl}$	 (85)	271

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

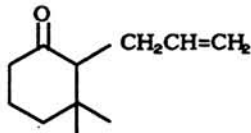
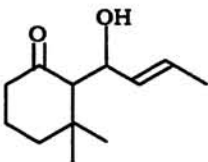

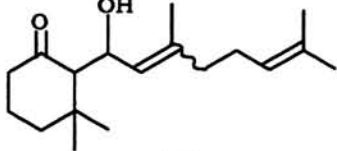
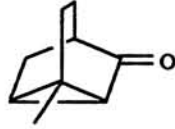
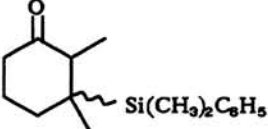
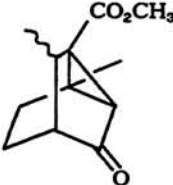
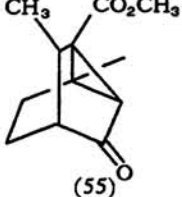
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
400		CH_3MgI , cat. CuI , -5°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, HMPA	 (55)	271
		CH_3MgI , cat. CuI , -5°	(<i>E</i>)- $\text{CH}_3\text{CH}=\text{CHCHO}$	 (90)	271
		CH_3MgI , cat. CuI , -5°	 CHO	 (96)	271
		1) THF, LDA 2) HMPA 3) $\text{CH}_2=\text{CHSO}_2\text{C}_6\text{H}_4\text{Cl-}p$	Intramolecular	 (19)	142
		$[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{CuLi}$, THF	CH_3I	 (-)	373
401		1) LDA, HMPA, THF, -19° 2) $\text{CH}_3\text{CH}=\text{CBrCO}_2\text{CH}_3$	Intramolecular	 (55)	368
		1) LDA 2) $Z\text{-CH}_3\text{CH}=\text{CBrCO}_2\text{CH}_3$	Intramolecular	 (55)	369

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
402		1) LDA 2)	Intramolecular	 (64)	372
		1) LDA 2)	Intramolecular	 (61)	374
		1) LDA 2)	Intramolecular	 79%	374
403		$(\text{CH}_3)_2\text{CuLi}, 0^\circ$	$\text{CH}_3\text{O}_2\text{CCl}$	 (54)	273
		1) LDA 2) $\text{CH}_2=\text{CBrCO}_2\text{CH}_3$	Intramolecular	 (56)	369
		$(\text{CH}_3)_2\text{CuLi}, 0^\circ$	$\text{CH}_3\text{I}, 1/1 \text{ THF/HMPA}$	 (95)	232

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

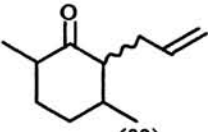
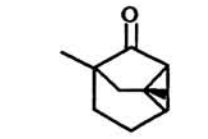

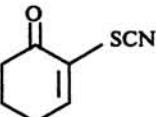
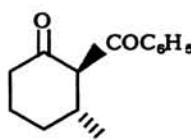
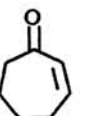
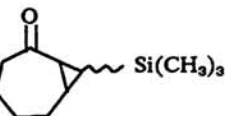

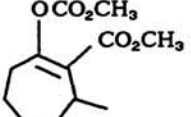
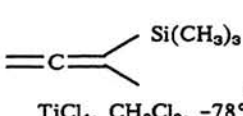

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{CH}_2=\text{CHCH}_2\text{I}$, 1/1 THF/HMPA	(89)	232
		1) LDA, THF 2) $\text{CH}_2=\text{C}(\text{CH}_3)\text{P}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	Intramolecular	(44)	176
		1) LDA, THF 2) $\text{CH}_2=\text{C}(\text{CH}_3)\text{P}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$, pyridine	Intramolecular	(44)	175
		$(\text{CH}_3)_2\text{CuLi}$, -70°	$\text{C}_6\text{H}_5\text{COCl}$	 (51)	296
		$(\text{CH}_3)_3\text{Si}-\text{C}(\text{CH}_3)=\text{C}-\text{Li}$ $(\text{CH}_3)_2\text{Si}^+$ THF, -30° to 15°	Intramolecular	 (40)	157
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{CH}_3\text{O}_2\text{CCl}$	 (47)	273
		TiCl_4 , CH_2Cl_2 , -78°	Intramolecular	 83:17 <i>cis:trans</i> (90-94)	214

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

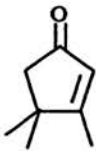
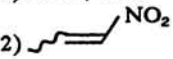
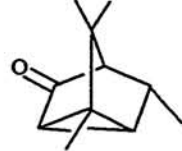
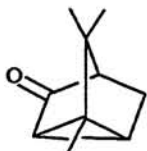
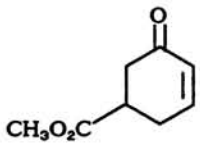
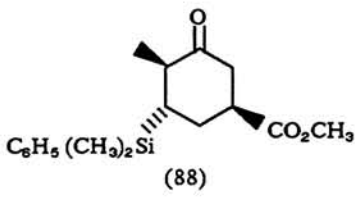
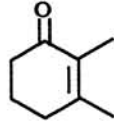
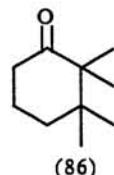
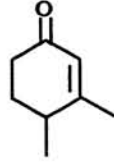
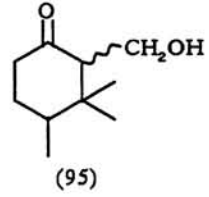
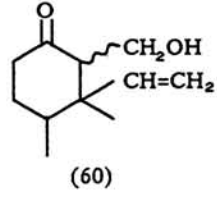
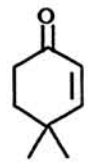
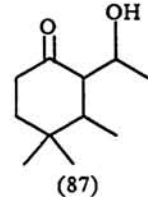
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
8		1) LDA, THF 2) 	Intramolecular	 (39)	179
		1) LDA, THF 2) $\text{CH}_2=\text{CHNO}_2$	Intramolecular	 (22)	179
		$[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{CuLi}$, THF, -23°	CH_3I , HMPA, -23°	 (88)	63
		$(\text{CH}_3)_2\text{CuLi}$, 0°	CH_3I , DME	 (86)	221
		CH_3MgI , CuI	H_2CO	 (95)	314
		$\text{CH}_2=\text{CHCu}$, $(n\text{-C}_4\text{H}_9)_3\text{P}$, -70° to 0°	H_2CO	 (60)	292
		$(\text{CH}_3)_2\text{CuLi}$, 0°	ZnCl_2 , CH_3CHO	 (87)	234

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

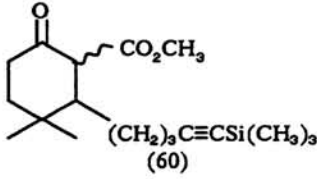
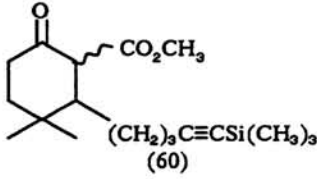
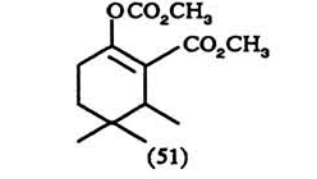
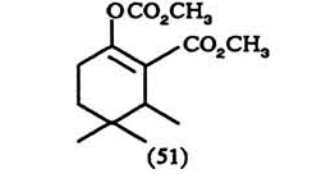
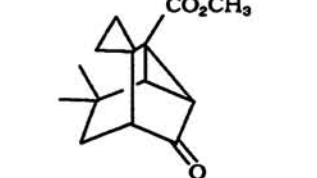
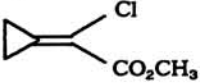
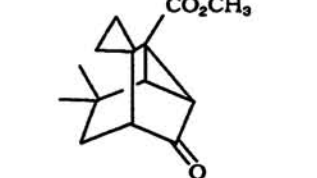
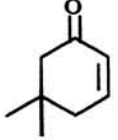
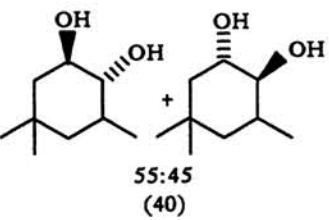
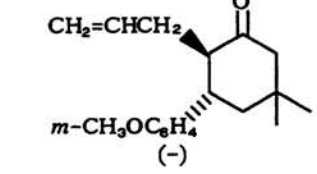
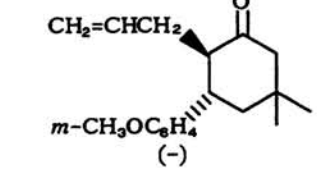
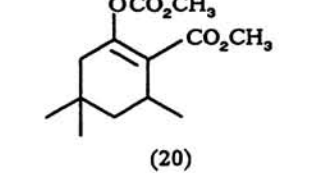
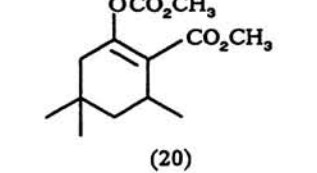
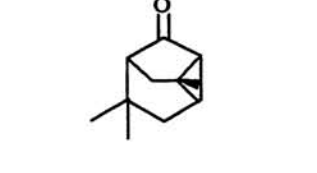
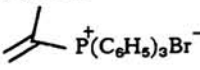
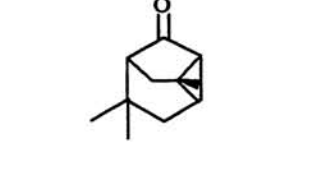
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(\text{CH}_3)_3\text{SiC}\equiv\text{C}(\text{CH}_2)_3\text{MgI}$, 7 mol % CuCN, -23°	$\text{CH}_3\text{O}_2\text{CCl}$, freshly distilled	 (60)	375 79
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{CH}_3\text{O}_2\text{CCl}$	 (51)	273
		1) LDA 2) 	Intramolecular	 (52)	372
		$(\text{CH}_3)_2\text{CuLi}$, -10°	$\text{BH}_3 \cdot \text{THF}$	 55:45 (40)	346
		$m\text{-CH}_3\text{OC}_6\text{H}_4\text{MgBr}$, cat. CuCl, 0° , $(\text{C}_2\text{H}_5)_2\text{O}/\text{THF}$	$\text{CH}_2=\text{CHCH}_2\text{Br}$, 40% HMPA	 $m\text{-CH}_3\text{OC}_6\text{H}_4$ (-)	26
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{CH}_3\text{O}_2\text{CCl}$	 (20)	273
		1) LDA, THF 2) 	Intramolecular	 (42)	176

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

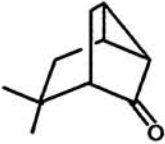
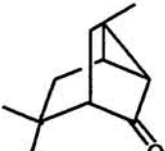
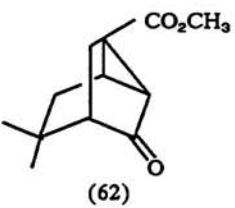
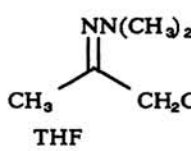
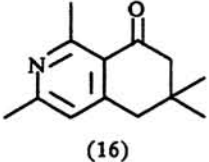
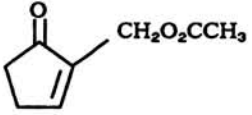
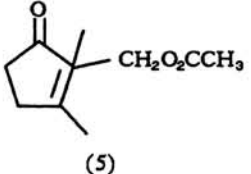
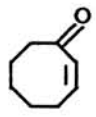
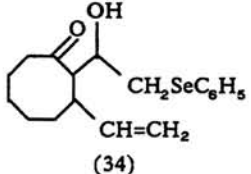
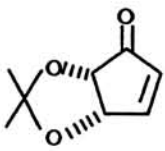
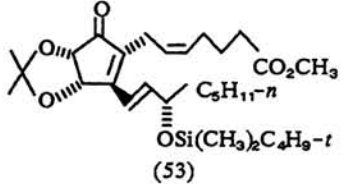
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		1) LDA, THF 2) $\text{CH}_2=\text{CHP}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	Intramolecular	 (13)	175
		1) LDA, THF 2) $\text{CH}_2=\text{C}(\text{CH}_3)\text{P}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	Intramolecular	 (13)	175
		1) LDA 2) $\text{CH}_2=\text{CBrCO}_2\text{CH}_3$	Intramolecular	 (62)	369
		$\text{CH}_2\text{Cu}(\text{SC}_6\text{H}_5)_2\text{Li}$, THF	1) CH_3COCN 2) H_3O^+	 (16)	299
		$(\text{CH}_3)_2\text{CuLi}$	CH_3I	 (5)	376
		$(\text{CH}_2=\text{CH})_2\text{CuMgBr}$, THF/ $(\text{C}_2\text{H}_5)_2\text{O}$, -45°	$\text{C}_6\text{H}_5\text{SeCH}_2\text{CHO}$	 (34)	377
		$n\text{-C}_9\text{H}_{17}\text{Si}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ THF, -78°	$\text{CuP}(\text{C}_4\text{H}_9\text{-}n)_3$ $\text{I}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ HMPA, -30°	 (53)	237

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

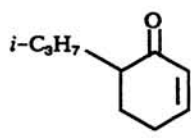
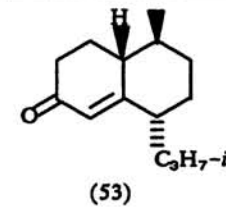
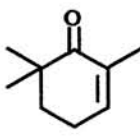
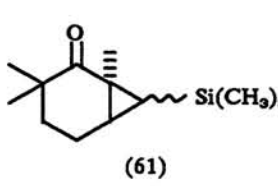
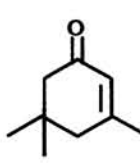
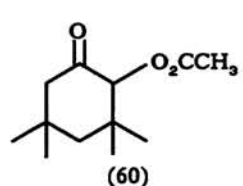
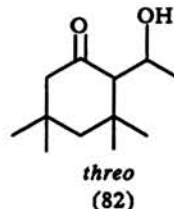
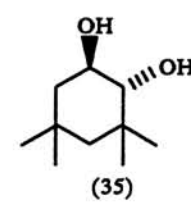
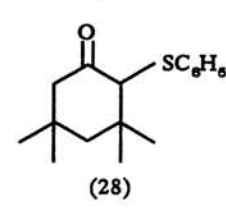
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
9		$(\text{CH}_3)_2\text{CuLi}$, 0°	1) $(\text{CH}_3)_3\text{Si}-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)_2$ 2) 2% KOH/ CH_3OH , reflux	 (53)	291
		$(\text{CH}_3)_3\text{Si}-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)_2$ Li $(\text{CH}_3)_2\text{Si}^+$, THF, -30° to 15°	Intramolecular	 (61)	157
		CH_3MgBr , cat. $\text{Cu}(\text{O}_2\text{CCH}_3)$, rt	$\text{Pb}(\text{O}_2\text{CCH}_3)_4$, C_6H_6	 (60)	378
		$(\text{CH}_3)_2\text{CuLi}$, 0°	ZnCl_2 , CH_3CHO	 <i>threo</i> (82)	234 220
		CH_3MgBr , cat. CuCl , -10°	1) $\text{BH}_3 \cdot \text{THF}$ 2) alkaline H_2O_2	 (35)	346
		$(\text{CH}_3)_2\text{CuLi}$, -10°	1) $\text{BH}_3 \cdot \text{THF}$ 2) alkaline H_2O_2	" (53)	346
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$(\text{C}_6\text{H}_5)_2\text{S}_2$	 (28)	182

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

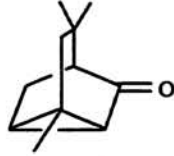
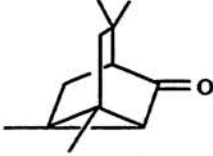
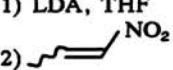
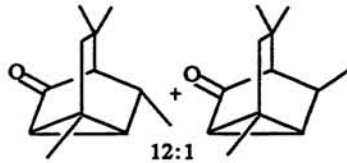
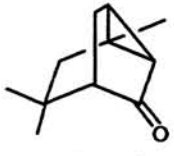
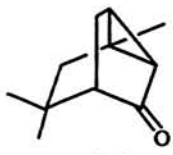
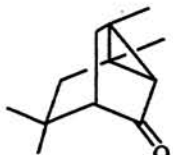
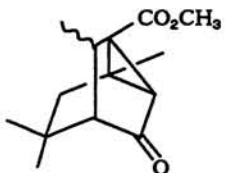
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		1) LDA, THF 2) HMPA 3) $\text{CH}_2=\text{CHSO}_2\text{C}_6\text{H}_5$, rt	Intramolecular	 (38)	142
		1) LDA, THF 2) HMPA 3) $\text{CH}_2=\text{C}(\text{CH}_3)\text{SO}_2\text{C}_6\text{H}_5$, rt	Intramolecular	 (21)	142
		1) LDA, THF 2) 	Intramolecular	 12:1 (63)	179
		1) LDA, THF 2) $\text{CH}_2=\text{CHP}^+(\text{C}_6\text{H}_6)_3\text{Br}^-$	Intramolecular	 (16-22)	174 175
		1) LDA, THF 2) $\text{CH}_2=\text{CHSO}_2\text{C}_6\text{H}_5$	Intramolecular	 (38)	379
		1) LDA, THF 2) $\text{CH}_2=\text{C}(\text{CH}_3)\text{SO}_2\text{C}_6\text{H}_5$	Intramolecular	 (21)	379
		1) LDA, HMPA, THF, -19° 2) $\text{CH}_3\text{CH}=\text{CBrCO}_2\text{CH}_3$	Intramolecular	 (20)	368

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

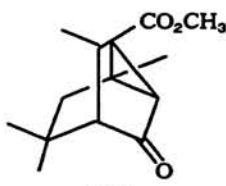
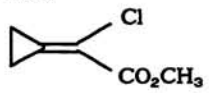
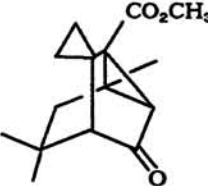
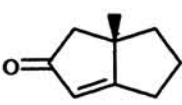
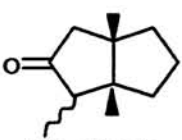
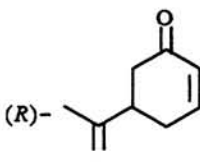
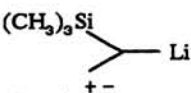
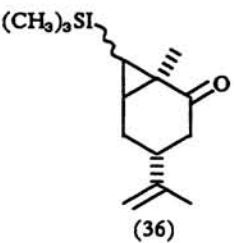
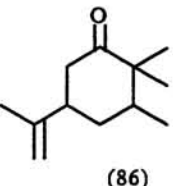
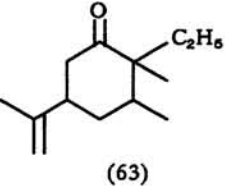
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
416		1) LDA 2) (z)-CH ₃ CH=CBrCO ₂ CH ₃	Intramolecular	 (20)	369
		1) LDA 2) 	Intramolecular	 (75)	372
		(CH ₃) ₂ CuLi, THF, -78°	CH ₂ =CHCH ₂ Cl, HMPA, rt	 CH ₂ CH=CH ₂ 3:2 mixture of isomers (74)	380 381
417		(CH ₃) ₃ Si-  (CH ₃) ₂ Si ⁻ , THF, -30° to 15°	Intramolecular	 (36)	157
		(CH ₃) ₂ CuLi, 0°, 45 min	CH ₃ I, DME, 0°, 5 min	 (86)	221
		(CH ₃) ₂ CuLi, 0°, 45 min	C ₂ H ₅ I, DME, 25°, 4h	 (63)	221

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

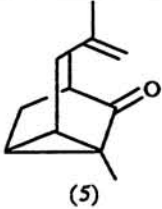
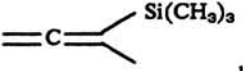
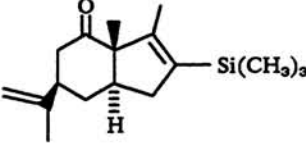
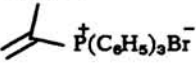
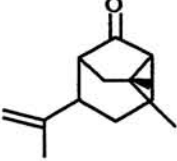
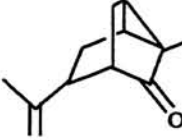
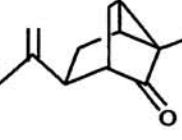
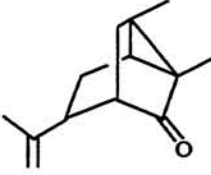
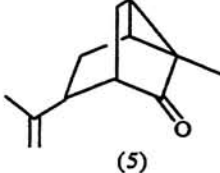
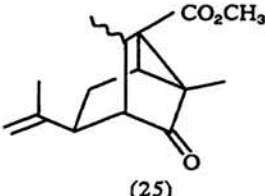
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		1) LDA, THF 2) HMPA 3) $\text{CH}_2=\text{CHSO}_2\text{C}_6\text{H}_5$	Intramolecular	 (5)	142
		$\text{TiCl}_4, \text{CH}_2\text{Cl}_2, -78^\circ$	Intramolecular	 (87)	214
		1) LDA, THF 2) 	Intramolecular	 (45)	176
		1) LDA, THF 2) $\text{CH}_2=\text{CHF}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	Intramolecular	 (32)	174
		1) LDA, THF 2) $\text{CH}_2=\text{CHF}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	Intramolecular	 (2)	175
		1) LDA, THF 2) $\text{CH}_2=\text{C}(\text{CH}_3)\text{F}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	Intramolecular	 (44)	175
		1) LDA, THF 2) $\text{CH}_2=\text{CHSO}_2\text{C}_6\text{H}_5$	Intramolecular	 (5)	379
		1) LDA, THF, HMPA, -19° 2) $\text{CH}_3\text{CH}=\text{CBrCO}_2\text{CH}_3$	Intramolecular	 (25)	368

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		1) LDA 2) Z-CH ₃ CH=CBrCO ₂ CH ₃	Intramolecular	 (25)	369
		1) LDA 2) CH ₂ =CBrCO ₂ CH ₃	Intramolecular	 (35)	369
10		 2.6 eq (<i>n</i> -C ₄ H ₉) ₃ P, -78°	CH ₃ O ₂ C(CH ₂) ₅ CHO	 mixture of isomers (83)	14
		 (<i>n</i> -C ₄ H ₉) ₃ P, -75°	CH ₃ O ₂ CCl, THF/HMPA	 (10)	268
		(CH ₃) ₂ AlSC ₆ H ₅ , CH ₂ Cl ₂ , -78°	Intramolecular	 (60)	204
		CH ₂ =CH(CH ₂) ₂ MgBr, 25 mol % CuBr, THF, -20° to -23°	Intramolecular	 (60)	382
		CH ₂ =CH(CH ₂) ₂ MgBr, CH ₂ =CHSO ₂ C ₆ H ₅ , 25 mol % CuBr, THF, -20° to -23°	Intramolecular	 (1)	142

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

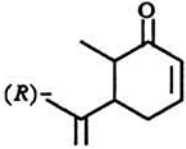
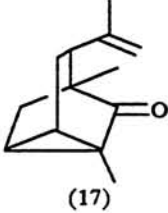

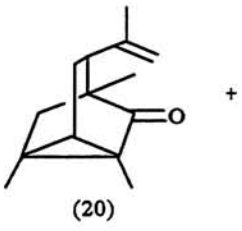
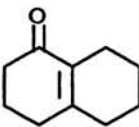
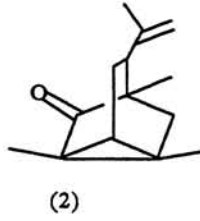
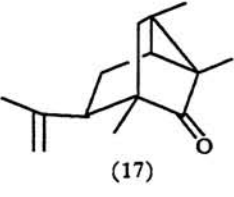
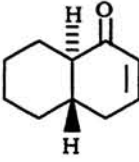
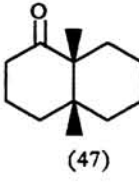
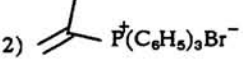
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
422		1) LDA, THF 2) HMPA 3) $\text{CH}_2=\text{CHSO}_2\text{C}_6\text{H}_5$	Intramolecular	 (17)	142
		1) LDA, THF 2) HMPA 3) $\text{CH}_2=\text{CHP}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	Intramolecular	" (65)	142
		1) LDA, THF 2) HMPA 3)  $\text{SO}_2\text{C}_6\text{H}_4\text{Cl-}p$	Intramolecular	 (20)	142
423		1) LDA, THF 2) $\text{CH}_2=\text{C}(\text{CH}_3)\text{SO}_2\text{C}_6\text{H}_5$	Intramolecular	 (2)	379
				 (17)	
423		$(\text{CH}_3)_2\text{CuLi}, 0^\circ$	$\text{CH}_3\text{I}, 1/1 \text{ THF/HMPA}$	 (47)	232
				1) LDA, THF 2)  $\text{P}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

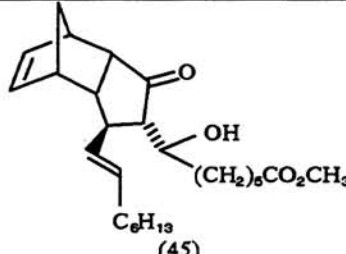
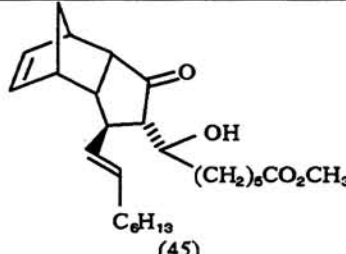
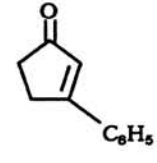
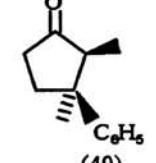
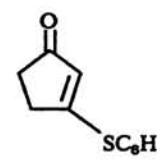
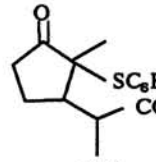
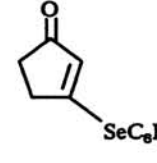
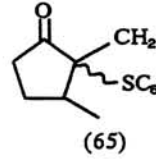
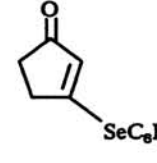
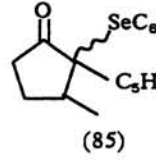
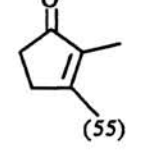
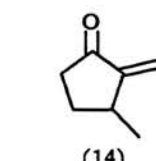
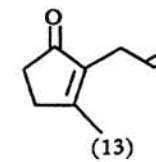
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
426		$(E)\text{-C}_6\text{H}_{13}\text{CH=CHMgBr}$, 2 mol % CuI, 0°	$\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_5\text{CHO}$, MgI ₂		74
11		$(\text{CH}_3)_2\text{CuLi}$, 0°	CH_3I , HMPA		316 67
		$\text{C}_2\text{H}_5\text{O}_2\text{CCH}(\text{CH}_3)\text{Li}$, CuI • P(OCH ₃) ₃	CH_3I		90
		$(\text{CH}_3)_2\text{CuLi}$, "chilled"	$\text{C}_2\text{H}_5\text{C}\equiv\text{CCH}_2\text{Br}$, DME		125
		$(\text{CH}_3)_2\text{CuLi}$, -20°	$n\text{-C}_8\text{H}_{17}\text{I}$, THF/HMPA		383
427		$(\text{CH}_3)_2\text{CuLi}$, -20°	1) CH_3X , THF/HMPA 2) O_3 3) $(\text{C}_2\text{H}_5)_2\text{NH}$, CH_2Cl_2		+ 384
					(14)
		$(\text{CH}_3)_2\text{CuLi}$, -20°	1) $\text{CH}_2=\text{CHCH}_2\text{X}$, THF/HMPA 2) O_3 3) $(\text{C}_2\text{H}_5)_2\text{NH}$, CH_2Cl_2		+ 384

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

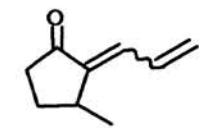
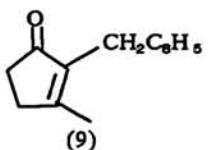
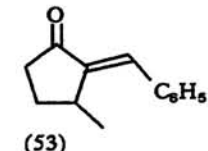
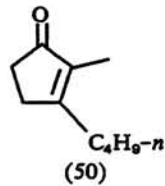
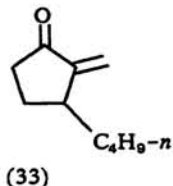
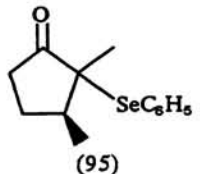
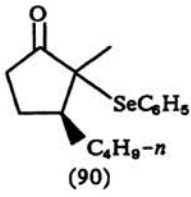
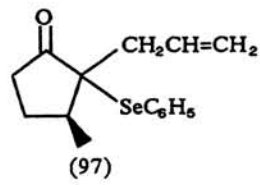
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
					
428		$(\text{CH}_3)_2\text{CuLi}$, -20°	1) $\text{C}_6\text{H}_5\text{CH}_2\text{X}$, THF/HMPA 2) O_3 3) $(\text{C}_2\text{H}_5)_2\text{NH}$, CH_2Cl_2	 +	384
					
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, -20°	1) CH_3X , THF/HMPA 2) O_3 3) $(\text{C}_2\text{H}_5)_2\text{NH}$, CH_2Cl_2	 +	384
					
		$(\text{CH}_3)_3\text{CuLi}$	CH_3I , HMPA, THF		230
429		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$	CH_3I , HMPA, THF		230
		$(\text{CH}_3)_2\text{CuLi}$	$\text{CH}_2=\text{CHCH}_2\text{Br}$, HMPA, THF		230

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

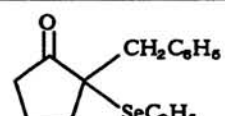
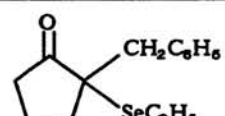
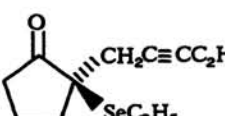
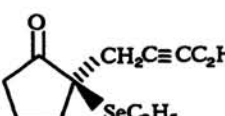
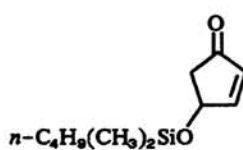
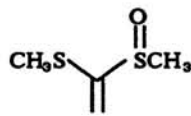
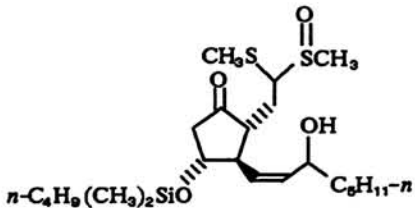
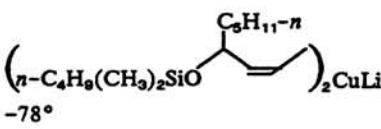
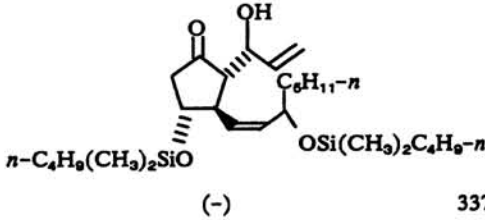
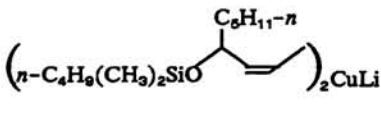
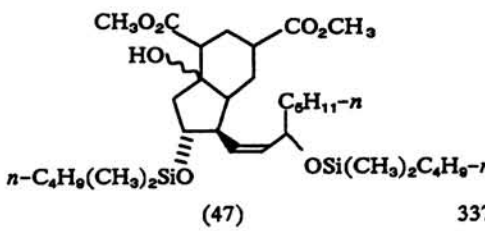
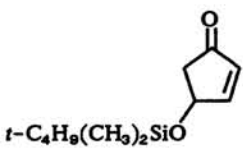
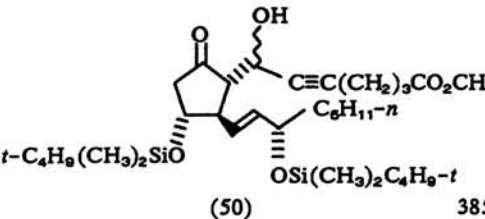
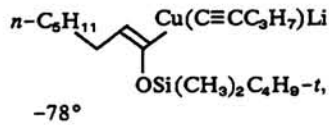
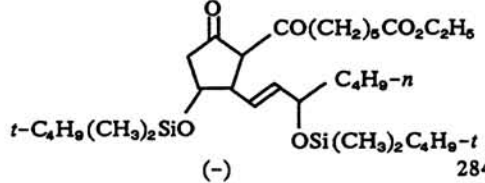
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(\text{CH}_3)_2\text{CuLi}$	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, HMPA, THF	 (90)	230
		$(\text{CH}_3)_2\text{CuLi}$	$\text{BrCH}_2\text{C}\equiv\text{CC}_2\text{H}_5$, HMPA, THF	 (96)	230
		$(\text{CH}_3\text{O})_2\text{C}(\text{C}_6\text{H}_{11-n})\text{O}_2\text{CuLi}$, -78°		 (53)	337
		$(\text{CH}_3\text{O})_2\text{C}(\text{C}_6\text{H}_{11-n})\text{O}_2\text{CuLi}$, -78°	$\text{CH}_2=\text{CHCHO}$	 (-)	337
		$(\text{CH}_3\text{O})_2\text{C}(\text{C}_6\text{H}_{11-n})\text{O}_2\text{CuLi}$	$\text{CH}_2=\text{CHCO}_2\text{CH}_3$	 (47)	337
		$\text{Cu}-\text{C}(\text{C}_6\text{H}_{11-n})=\text{C}(\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9-t)$, 2.6 eq $(n\text{-C}_4\text{H}_9)_3\text{P}$, -78°	$\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_3\text{C}\equiv\text{CCHO}$	 (50)	385
		$n\text{-C}_6\text{H}_{11}-\text{C}(\text{C}\equiv\text{CC}_3\text{H}_7)\text{CuLi}$, -78°	$\text{C}_2\text{H}_5\text{O}_2\text{C}(\text{CH}_2)_5\text{COCl}$, THF/HMPA	 (-)	284

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$\text{Cu}(\text{C}\equiv\text{CC}_6\text{H}_7)\text{Li}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9-t$ $(n\text{-C}_4\text{H}_9)_3\text{P}, -78^\circ$	$\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_6\text{COCl}$ $\text{HMPA}/\text{THF}, -40^\circ$	 trace of C-2 epimer (35)	112
		$\text{Cu}(\text{C}\equiv\text{CC}_6\text{H}_7)\text{Li}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9-t$ -78°	$\text{C}_2\text{H}_5\text{O}_2\text{C}(\text{CH}_2)_5\text{COCl}$ THF/HMPA	 (23)	112
		Li SOC_6H_5 $\text{THF}, -76^\circ$	$\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_5\text{CHO}$	 (68)	152
		Li SOC_6H_5 $\text{THF}, -76^\circ$	$\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9-t$	 (70)	152
		Li SOC_6H_5	$\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9-t$	 (62)	152
		$(n\text{-C}_4\text{H}_9)_3\text{PCu}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9-t$ $\text{HMPA}, (\text{C}_6\text{H}_5)_3\text{SnCl}, -78^\circ$	$\text{I}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ -25°	 (78)	89

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		HMPA, $(C_6H_5)_3SnCl$, -78°	$I(CH_2)_6CO_2CH_3$, $\sim -25^\circ$	 (20)	89
		HMPA, $(C_6H_5)_3SnCl$, -78°	$I-C\equiv C-CH_2-CH_2-CO_2CH_3$, $\sim -25^\circ$	 (82)	89
		HMPA, $(C_6H_5)_3SnCl$, -78°	$I-C\equiv C-CH_2-CH_2-CO_2CH_3$, $\sim -25^\circ$	 (77)	89
		-78°		 (42)	285
		$(CH_3)_3Si$ $(CH_3)_3Si^+ Li^-$, THF, -30° to 15°	Intramolecular	 (44)	157
		$(CH_3)_2CuLi$, -60°	Intramolecular	 (63)	350
		$CuBr \cdot DMS$, THF, -78°	HCl , H_2O , THF	 (71)	278

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

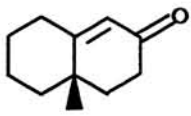
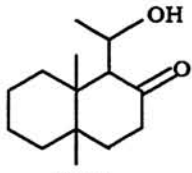
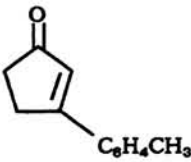
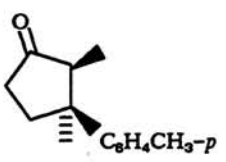
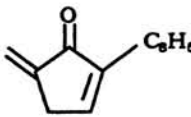
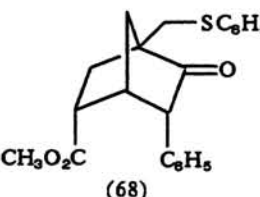
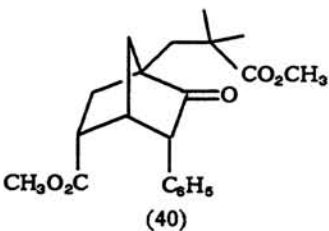
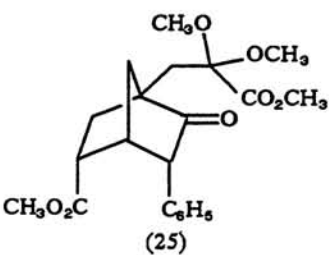
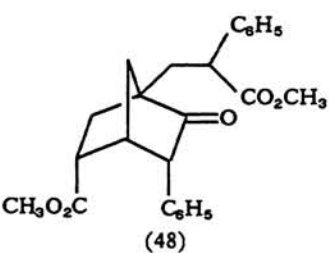
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(\text{CH}_3)_2\text{CuLi}$, 0°	ZnCl_2 , CH_3CHO	 <i>threo</i> (76)	234 220
12		$(\text{CH}_3)_2\text{CuLi}$	CH_3I	 (62)	316
		$\text{C}_6\text{H}_5\text{SLi}$, THF, -78°	Methyl acrylate	 (68)	136
		$\text{CH}_3\text{O}_2\text{CC}(\text{CH}_3)_2\text{Li}$, THF, -78°	Methyl acrylate	 (40)	136
		$\text{CH}_3\text{O}_2\text{CC}(\text{OCH}_3)_2\text{Li}$, THF, -78°	Methyl acrylate	 (25)	136
		$\text{CH}_3\text{O}_2\text{CCH}(\text{C}_6\text{H}_5)\text{Li}$, THF, -78°	Methyl acrylate	 (48)	136

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
438		$\text{CH}_3\text{O}_2\text{CC}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Li}$, THF, -78°	Methyl acrylate	 (41)	136
		THF, -78°	Methyl acrylate	 (41)	136
		$(\text{CH}_3)_2\text{CuLi}$, -20°	1) CH_3X , THF/HMPA 2) O_3 3) $(\text{C}_2\text{H}_5)_2\text{NH}$, CH_2Cl_2	 (51) +	384
				 (22)	
439		$(\text{CH}_3)_2\text{CuLi}$	CH_3I , HMPA, THF	 (78)	230
		$(\text{CH}_3)_2\text{CuLi}$	$\text{BrCH}_2\text{C}\equiv\text{CC}_2\text{H}_5$, HMPA, THF	 (90)	230

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

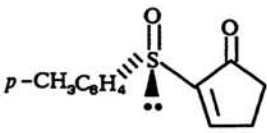
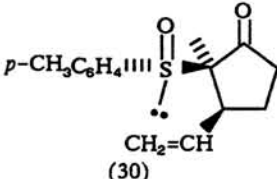
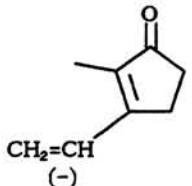
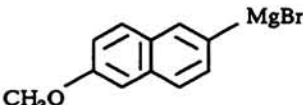
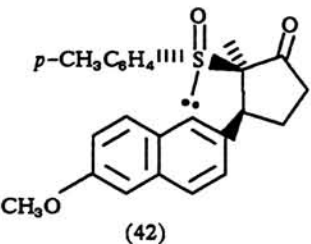
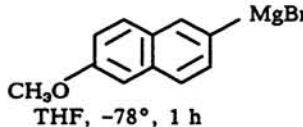
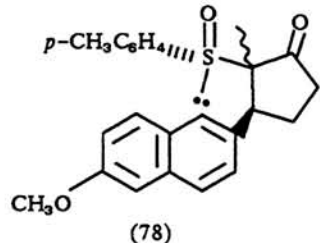
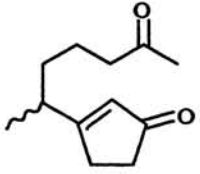
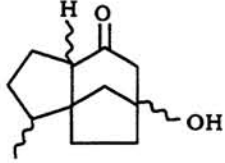
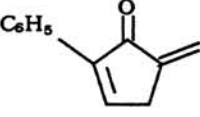
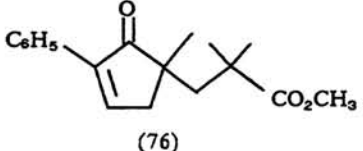
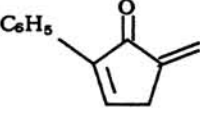
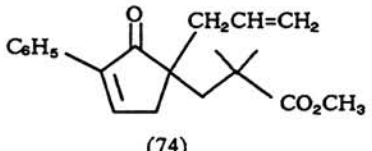
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$\text{CH}_2=\text{CHMgBr}$, ZnBr_2 , THF, -78°	CH_3I , HMPA	 (30) +  (-)	386
		MgBr THF, -78°	CH_3I , HMPA, 33° , 24 h	 (42)	387
		MgBr THF, -78° , 1 h	CH_3I , NMP	 (78)	192
		NaOH , 3 eq $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$, rt	Intramolecular	 (-)	123
		$\text{CH}_3\text{O}_2\text{C}(\text{CH}_3)_2\text{CLi}$, THF, -78°	CH_3I	 (76)	135
		$\text{CH}_3\text{O}_2\text{C}(\text{CH}_3)_2\text{CLi}$, THF, -78°	$\text{CH}_2=\text{CHCH}_2\text{Br}$	 (74)	135

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

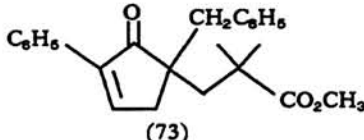
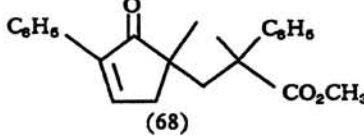
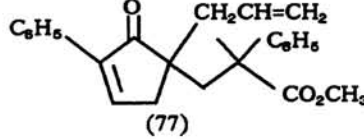
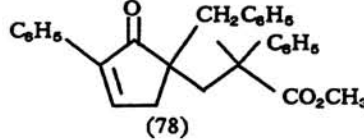
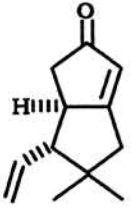
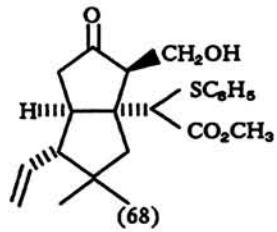
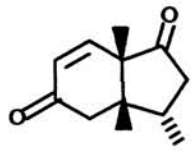
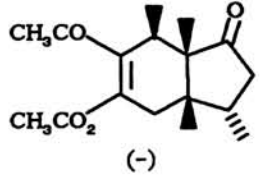
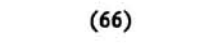
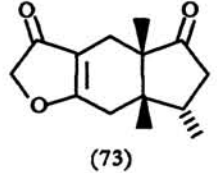
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$\text{CH}_3\text{O}_2\text{CC}(\text{CH}_3)_2\text{CLi}$, THF, -78°	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	 (73)	135
		$\text{CH}_3\text{O}_2\text{CC}(\text{CH}_3)\text{C}_6\text{H}_5\text{Li}$, THF, -78°	CH_3I	 (68)	135
		$\text{CH}_3\text{O}_2\text{CC}(\text{CH}_3)\text{C}_6\text{H}_5\text{Li}$, THF, -78°	$\text{CH}_2=\text{CHCH}_2\text{Br}$	 (77)	135
		$\text{CH}_3\text{O}_2\text{CC}(\text{CH}_3)\text{C}_6\text{H}_5\text{Li}$, THF, -78°	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	 (78)	135
		$\text{C}_6\text{H}_5\text{S}-\text{C}(\text{CH}_3)_2-\text{Li}$, CO_2CH_3 , THF, -60° to -35°	H_2CO , -60°	 (68)	281
		$(\text{CH}_3)_2\text{CuLi}$, 25°	CH_3COCl	 (-)	272
		$(\text{CH}_3)_2\text{CuLi}$	CH_3COCl	 (66)	269
		$(\text{CH}_3)_2\text{CuLi}$	ClCH_2COCl	 (73)	269

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$(\text{CH}_2=\text{CH})_2\text{CuMgBr}$, -50°	H_2CO	 (65)	388
		1) LDA 2) $\text{CH}_2=\text{CBrCO}_2\text{CH}_3$	Intramolecular	 (20) + (12)	369
		$(\text{CH}_3)_2\text{CuLi}$, -40° to rt	Intramolecular	 (69)	317
		$n\text{-C}_4\text{H}_9\text{Li}$, $\text{Ni}(\text{CO})_4$, THF, -50°	$\text{CH}_2=\text{CHCH}_2\text{I}$, HMPA	 (85)	389
		$n\text{-C}_4\text{H}_9\text{Li}$, $\text{Ni}(\text{CO})_4$, THF, -50°	$n\text{-C}_3\text{H}_7\text{I}$, HMPA	 (21)	389

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

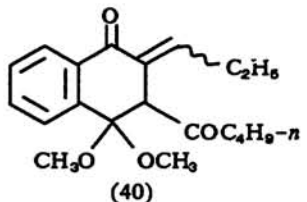
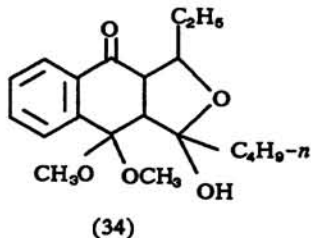
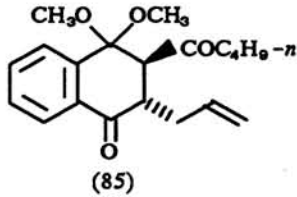
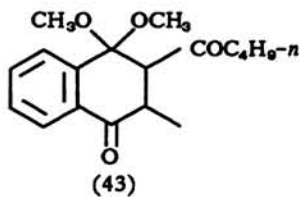
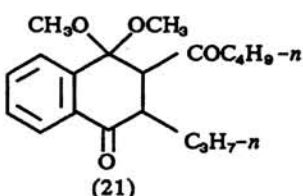
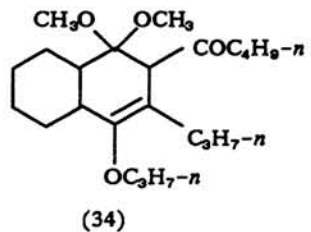
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$n\text{-C}_4\text{H}_9\text{Li}, \text{Ni}(\text{CO})_4,$ THF, -50°	$\text{C}_2\text{H}_5\text{CHO}$	 (40)	389
				 (34)	
		$n\text{-C}_4\text{H}_9\text{CONi}(\text{CO})_n,$ THF	$\text{CH}_2=\text{CHCH}_2\text{I}, \text{HMPA}$	 (85)	212
		$n\text{-C}_4\text{H}_9\text{CONi}(\text{CO})_n,$ THF	$\text{CH}_3\text{I}, \text{HMPA}$	 (43)	212
		$n\text{-C}_4\text{H}_9\text{CONi}(\text{CO})_n,$ THF	$\text{C}_3\text{H}_7\text{I}, \text{HMPA}$	 (21)	212
				 (34)	

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

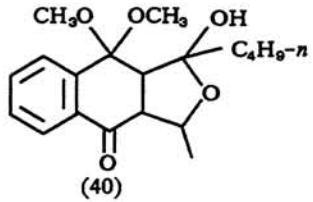
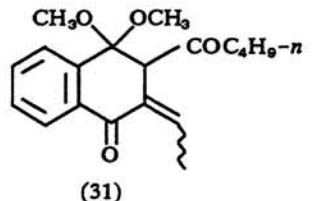
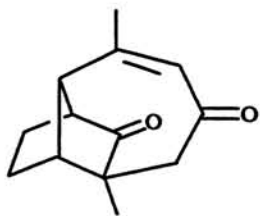
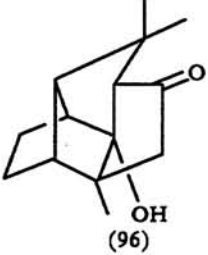
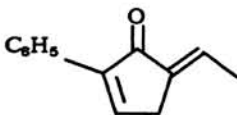
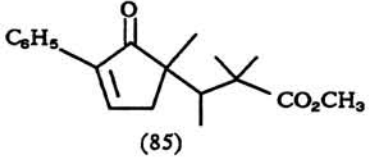
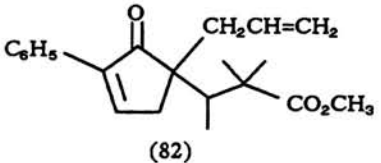
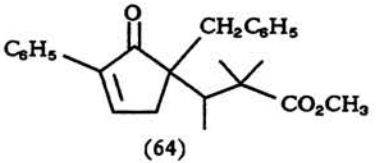
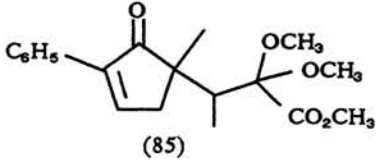
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$n\text{-C}_4\text{H}_9\text{CONi(CO)}_n$, THF	CH_3CHO	 (40)	212
				 (31)	
13		$(\text{CH}_3)_2\text{CuLi}$, -40° to rt	Intramolecular	 (96)	317
		$\text{CH}_3\text{O}_2\text{CC(CH}_3)_2\text{Li}$, THF, -78°	CH_3I	 (85)	135
		$\text{CH}_3\text{O}_2\text{CC(CH}_3)_2\text{Li}$, THF, -78°	$\text{CH}_2=\text{CHCH}_2\text{Br}$	 (82)	135
		$\text{CH}_3\text{O}_2\text{CC(CH}_3)_2\text{Li}$, THF, -78°	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	 (64)	135
		$\text{CH}_3\text{O}_2\text{CC(OCH}_3)_2\text{Li}$, THF, -78°	CH_3I	 (85)	135

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

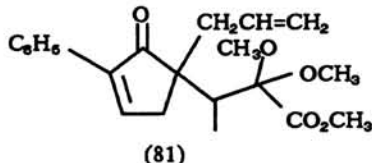
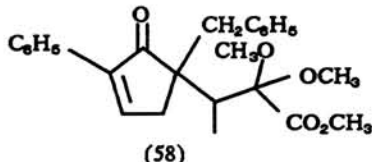
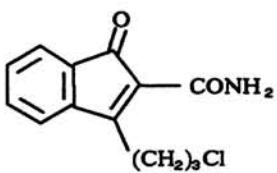
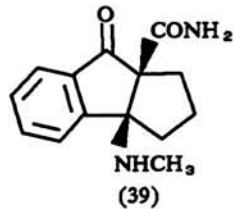
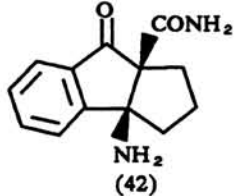
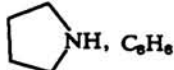
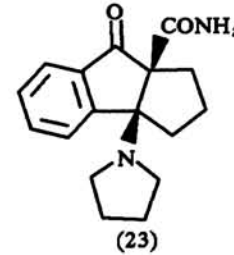
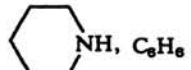
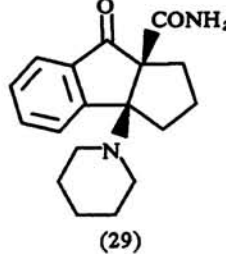
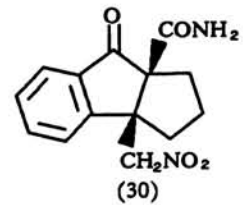
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
450		$\text{CH}_3\text{O}_2\text{CC}(\text{OCH}_3)_2\text{Li}$, THF, -78°	$\text{CH}_2=\text{CHCH}_2\text{Br}$	 (81)	135
		$\text{CH}_3\text{O}_2\text{CC}(\text{OCH}_3)_2\text{Li}$, THF, -78°	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	 (58)	135
		CH_3NH_2 , C_6H_6	Intramolecular	 (39)	147
		$\text{NH}_3(\text{l})$, C_6H_6	Intramolecular	 (42)	147
		NH , C_6H_6	Intramolecular	 (23)	147
451		NH , C_6H_6	Intramolecular	 (29)	147
		CH_3NO_2 , 10% NaOH/ $t\text{-C}_4\text{H}_9\text{OH}$	Intramolecular	 (30)	147

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

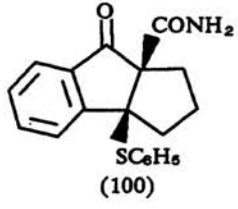
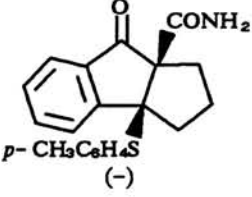
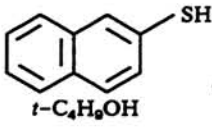
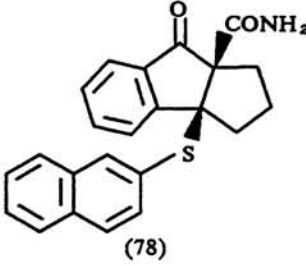
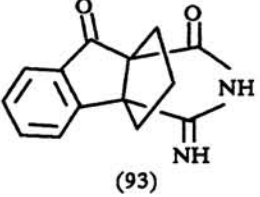
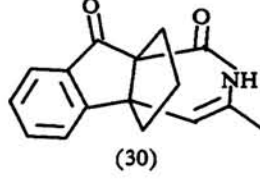
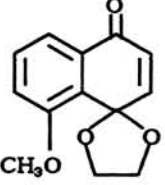

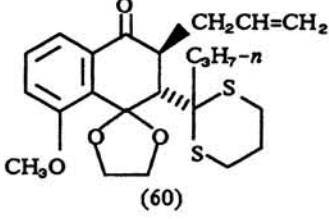
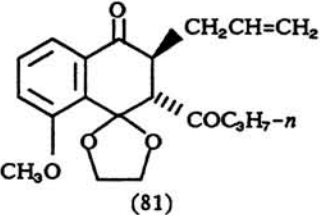
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		$C_6H_5SH, NaH, t-C_4H_9OH$	Intramolecular	 (100)	147
		$p-CH_3C_6H_4SH, NaH, t-C_4H_9OH$	Intramolecular	 $p-CH_3C_6H_4S$ (-)	147
		$NaH, t-C_4H_9OH$	Intramolecular	 (78)	147
		$NaCN, t-C_4H_9OH, H_2O, steam bath$	Intramolecular	 (93)	147
		$(CH_3)_2CO, 10\% KOH, t-C_4H_9OH$	Intramolecular	 (30)	147
		 $Li, C_3H_7-n, THF/HMPA$	$CH_2=CHCH_2Br$	 (60)	389
		$n-C_3H_7Li, Ni(CO)_4, THF$	$CH_2=CHCH_2I, HMPA$	 (81)	389

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

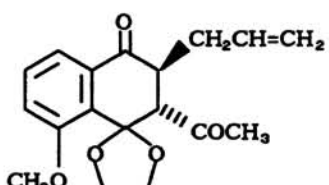
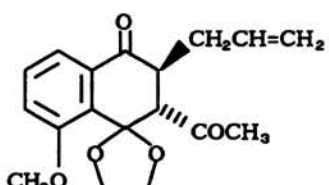
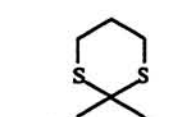
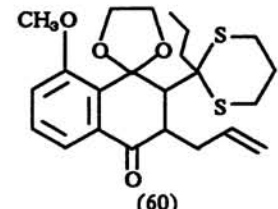
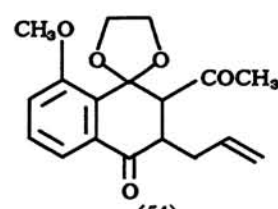
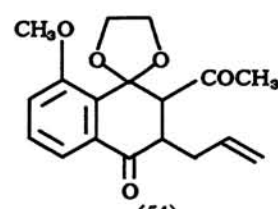
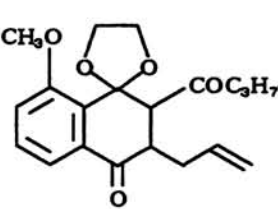
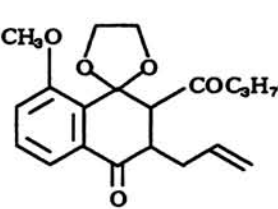

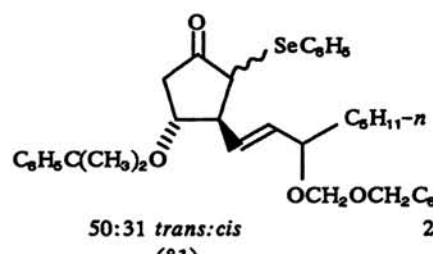

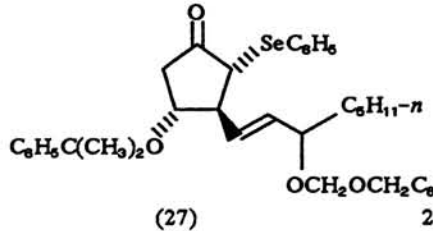
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		CH_3Li , $\text{Ni}(\text{CO})_4$, THF	$\text{CH}_2=\text{CHCH}_2\text{I}$, HMPA	 (54)	389
		$n\text{-C}_3\text{H}_7$ Li, THF, HMPA	$\text{CH}_2=\text{CHCH}_2\text{Br}$	 (60)	212
		$\text{CH}_3\text{CONi}(\text{CO})_n$	$\text{CH}_2=\text{CHCH}_2\text{I}$, HMPA	 (54)	212
		$n\text{-C}_3\text{H}_7\text{CONi}(\text{CO})_n$	$\text{CH}_2=\text{CHCH}_2\text{I}$, HMPA	 (82)	212
14		$\text{Cl}(\text{C}_6\text{H}_5)_2\text{Zr}$, $\text{C}_6\text{H}_{11-n}$, $\text{OCH}_2\text{OCH}_2\text{C}_6\text{H}_5$ THF, $\text{Ni}(\text{acac})_2$, $(i\text{-C}_4\text{H}_9)_2\text{AlH}$, 0°	$\text{C}_6\text{H}_5\text{SeBr}$, $(\text{C}_6\text{H}_5)_2\text{Se}_2$, -78°	 (81) 50:31 <i>trans:cis</i>	209
		$\text{Cl}(\text{C}_6\text{H}_5)_2\text{Zr}$, $\text{C}_6\text{H}_{11-n}$, $\text{OCH}_2\text{OCH}_2\text{C}_6\text{H}_5$ THF, $\text{Ni}(\text{acac})_2$, $(i\text{-C}_4\text{H}_9)_2\text{AlH}$, 0°	$\text{C}_6\text{H}_5\text{SeCl}$, -78°	 (27)	209

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
456		$\text{Cl}(\text{C}_6\text{H}_5)_2\text{Zr}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9-t$ $\text{Ni}^{+2}(\text{CH}_3\text{COCHCOCH}_3)_2,$ $(i\text{-C}_4\text{H}_9)_2\text{AlH}, 0^\circ$	H_2CO	 (70)	210
		$\text{Cl}(\text{C}_6\text{H}_5)_2\text{Zr}$ $\text{OCH}_2\text{OCH}_2\text{C}_6\text{H}_5$ $\text{Ni}^{+2}(\text{CH}_3\text{COCHCOCH}_3)_2,$ $(i\text{-C}_4\text{H}_9)_2\text{AlH}, \text{THF}, 0^\circ$	H_2CO	 (69)	210
		$\text{NaOH}, 3 \text{ eq}$ $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}, 25^\circ$	Intramolecular	 (38)	123
				 (11)	
		$(\text{CH}_3)_2\text{CuLi}, \text{THF}, 0^\circ$	Intramolecular	 (10)	73
		$\text{CH}_3\text{MgCl}, 10 \text{ mol } \%$ $\text{CuBr} \cdot \text{DMS}$	Intramolecular	 (15)	73

456

457

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

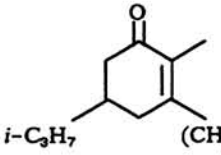
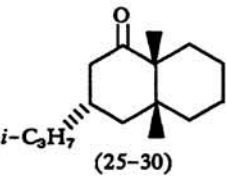
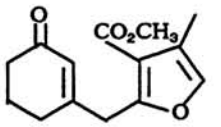
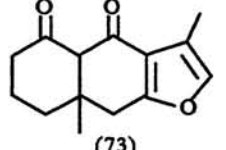
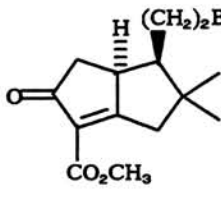
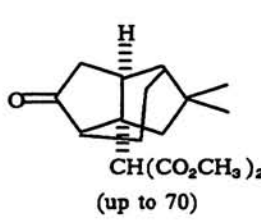
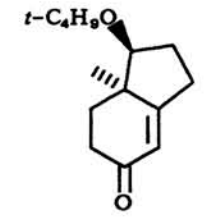
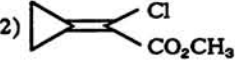
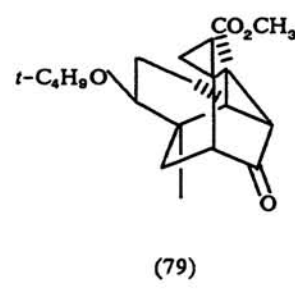
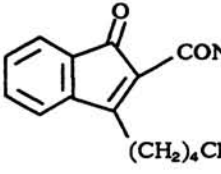
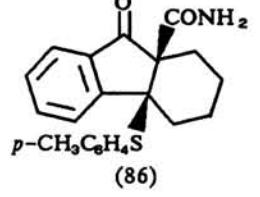
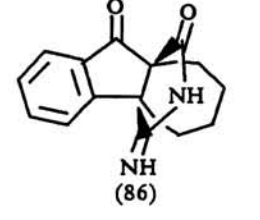
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
				"	
		$(\text{CH}_3)_2\text{MgCl} \cdot \text{DMS}$	Intramolecular	(25)	73
458		$(\text{CH}_3)_2\text{CuLi}, \text{C}_6\text{H}_6, 0^\circ \text{ to } 5^\circ$	HMPA, 0°	 (25-30)	108 118
		$(\text{CH}_3)_2\text{CuLi}, 0^\circ$	Intramolecular	 (73)	233
		$(\text{CH}_3\text{O}_2\text{C})_2\text{CHNa}, \text{THF}, \text{reflux}$	Intramolecular	 $\text{CH}(\text{CO}_2\text{CH}_3)_2$ (up to 70)	241
		1) LDA 2) 	Intramolecular	 (79)	372
459		$p\text{-CH}_3\text{C}_6\text{H}_4\text{SH}, \text{NaH}, \text{DMF}$	Intramolecular	 (86)	147
		$\text{NaCN}, t\text{-C}_4\text{H}_9\text{OH}, \text{H}_2\text{O}, \text{steam bath}$	Intramolecular	 (86)	147

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

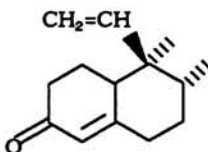
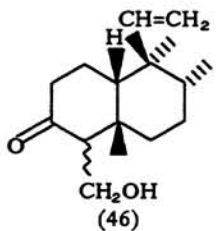
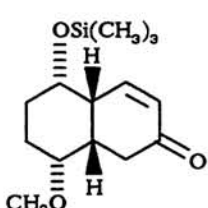
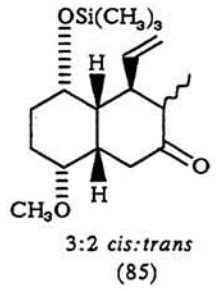
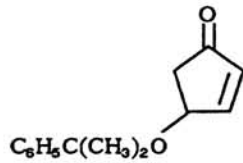
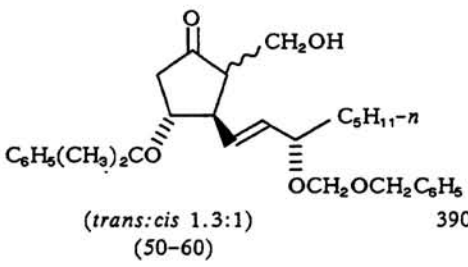
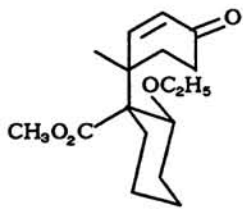
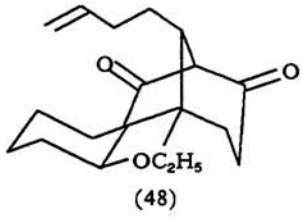
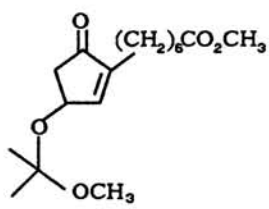
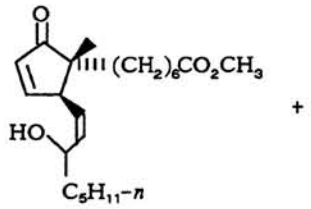
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
460		$(\text{CH}_3)_2\text{CuLi}$, DMS/ $(\text{C}_2\text{H}_5)_2\text{O}$ /pentane, -20°	H_2CO	 CH ₂ OH (46)	292
		$(\text{CH}_2=\text{CH})_2\text{CuLi}$	CH_3I	 OSi(CH ₃) ₃ CH ₃ O 3:2 cis:trans (85)	305
		$(n\text{-C}_5\text{H}_{11}\text{-CH}_2\text{-CH=CH})_2\text{CuLi}$, $(n\text{-C}_4\text{H}_9)_3\text{P}$, -78°	H_2CO	 CH ₂ OH C ₆ H ₅ (CH ₂) ₂ CO C ₅ H _{11-n} OCH ₂ OCH ₂ C ₆ H ₅ (trans:cis 1.3:1) (50-60)	390
461	17 	$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{MgBr}$, 25 mol % CuBr, THF, -20° to -23°	Intramolecular	 OC ₂ H ₅ (48)	382
		$(\text{CH}_3\text{O-C(CH}_3)_2\text{-O-CH}_2\text{-CH=CH-C}_5\text{H}_{11-n})_2\text{CuLi}$	1) CH_3I , 20% HMPA 2) H_3O^+	 HO (CH ₂) ₆ CO ₂ CH ₃ C ₅ H _{11-n}	337

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

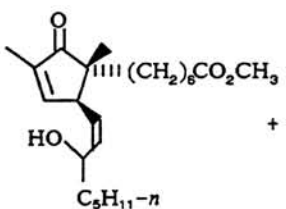
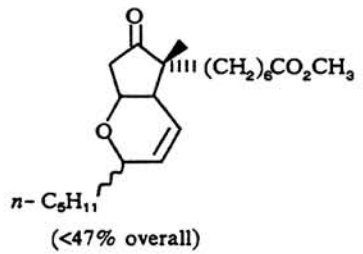
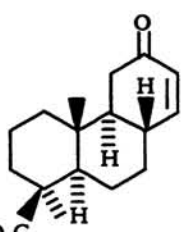
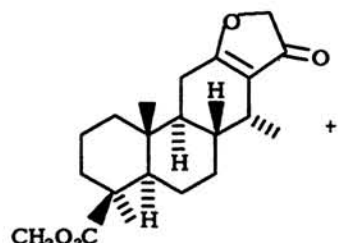
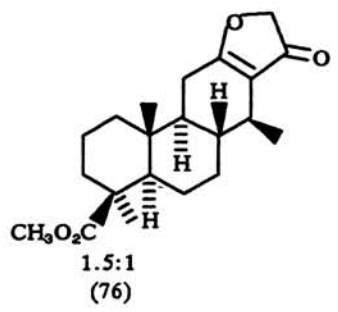
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
462				 (n -C ₅ H ₁₁ , <47% overall)	
18		(CH ₃) ₂ CuLi, -25°	1) ClCH ₂ COCl 2) base	 CH ₃ O ₂ C	269
463		(CH ₃) ₂ CuLi, -40°	1) ClCH ₂ COCl 2) base	 CH ₃ O ₂ C 1.5:1 (76)	269

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

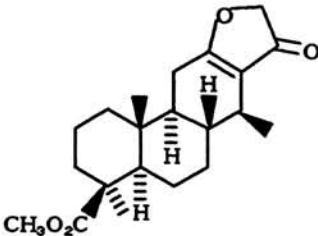
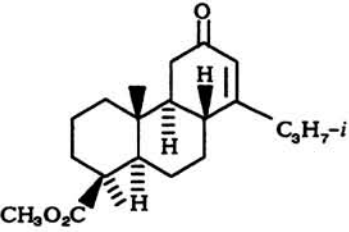
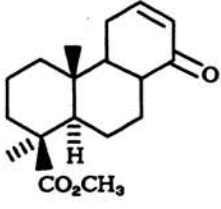
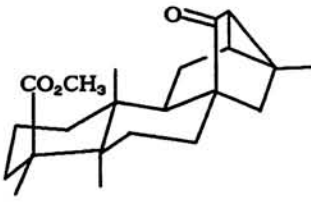
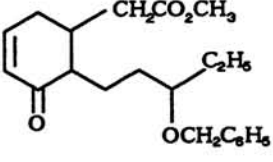
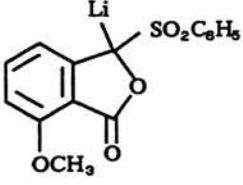
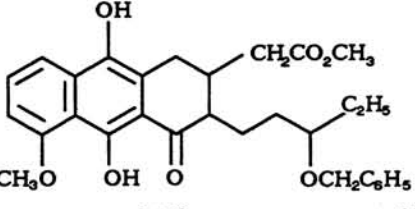
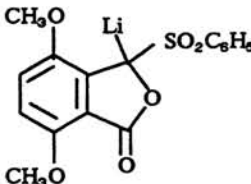
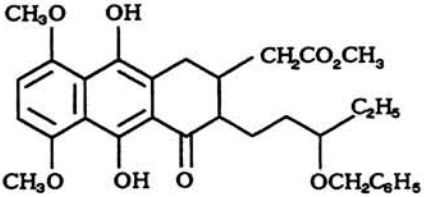
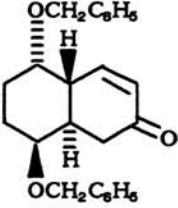
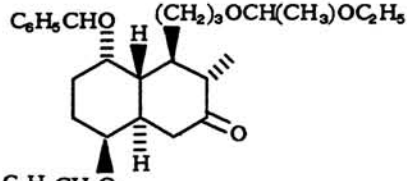
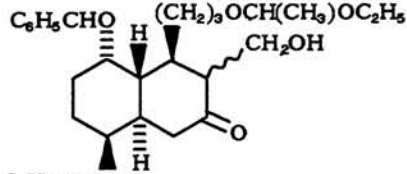
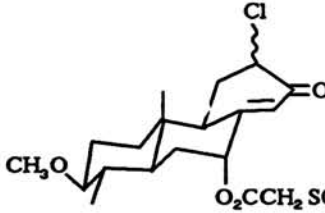
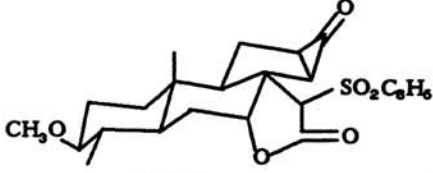
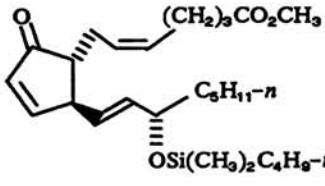
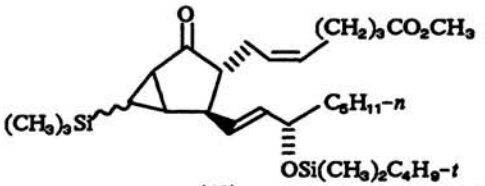
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
				2:1 (70.6)	
		$(i\text{-C}_3\text{H}_7)_2\text{CuLi}$, DMS, THF, -78°	1) $\text{C}_6\text{H}_5\text{SeCl}$ 2) $\text{H}_2\text{O}_2/\text{THF}$	 (55)	321
		1) LDA, THF 2) $\text{CH}_2=\text{C}(\text{CH}_3)\text{P}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	Intramolecular	 (20)	176
		1) LDA, THF 2) $\text{CH}_2=\text{C}(\text{CH}_3)\text{P}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	Intramolecular	" (23)	175
21			Intramolecular	 (~80)	153
			Intramolecular	 (~82)	153

TABLE I. α,β -UNSATURATED ALDEHYDES AND KETONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
24		$C_2H_5OCH(CH_3)O(CH_2)_3Cu(SC_6H_5)_2Li$, THF, -20°	CH_3I , DME	 (80)	391
		$C_2H_5OCH(CH_3)O(CH_2)_3Cu(SC_6H_5)_2Li$, THF, -20°	$H_2CO(g)$, -78°	 (67)	391
25		CsF , CH_2Cl_2 , 25°	Intramolecular	 (83-91)	130
27		$(CH_3)_3Si^-Li^+$, $(CH_3)_2Si^+Li^-$, THF, -30° to 15°	Intramolecular	 (40)	157

^a See addendum to Table IB for additional entries.

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES

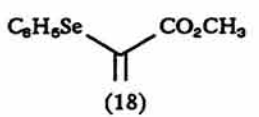
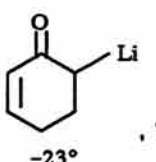
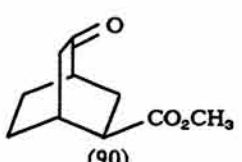
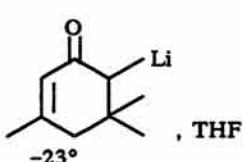
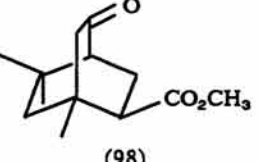
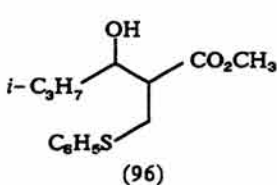
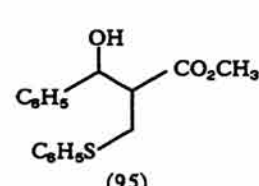
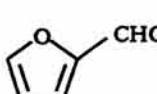
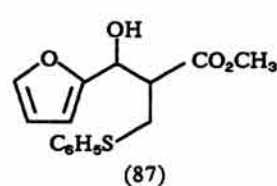
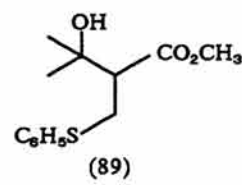
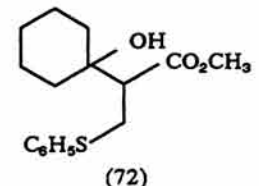
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
3	$\text{CH}_2=\text{CHCO}_2\text{CH}_3$	LDA, THF, 0°	$\text{C}_6\text{H}_5\text{SeBr}$	 (18)	203
		 -23°, THF,	Intramolecular	 (90)	139
		 -23°, THF,	Intramolecular	 (98)	139
		$\text{C}_6\text{H}_5\text{SMgI}$, $(\text{C}_2\text{H}_5)_2\text{O}/n\text{-C}_6\text{H}_{14}$, 0°	$i\text{-C}_3\text{H}_7\text{CHO}$	 (96)	145
		$\text{C}_6\text{H}_5\text{SMgI}$, $(\text{C}_2\text{H}_5)_2\text{O}/n\text{-C}_6\text{H}_{14}$, 0°	$\text{C}_6\text{H}_5\text{CHO}$	 (95)	145
		$\text{C}_6\text{H}_5\text{SMgI}$, $(\text{C}_2\text{H}_5)_2\text{O}/n\text{-C}_6\text{H}_{14}$, 0°		 (87)	145
		$\text{C}_6\text{H}_5\text{SMgI}$, $(\text{C}_2\text{H}_5)_2\text{O}/n\text{-C}_6\text{H}_{14}$, 0°	$(\text{CH}_3)_2\text{CO}$	 (89)	145
		$\text{C}_6\text{H}_5\text{SMgI}$, $(\text{C}_2\text{H}_5)_2\text{O}/n\text{-C}_6\text{H}_{14}$, 0°	Cyclohexanone	 (72)	145

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)


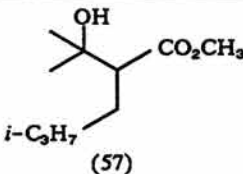
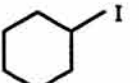
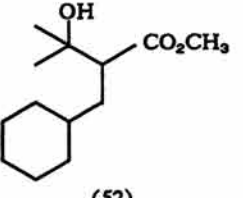
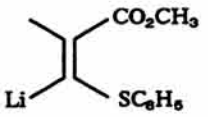
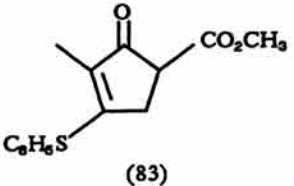
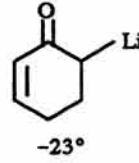
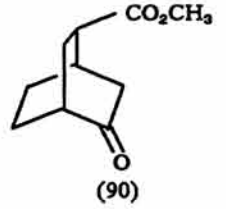
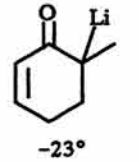
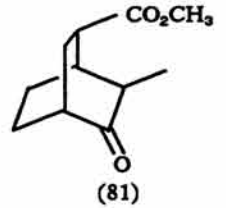
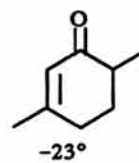
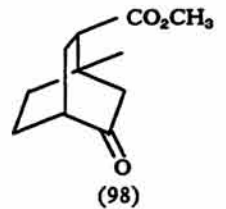
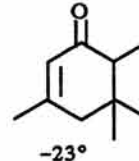
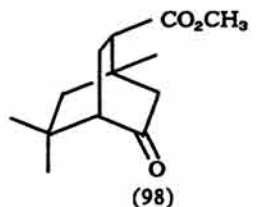
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		$i\text{-C}_3\text{H}_7\text{I}$, Zn, CH_3CN , reflux	$(\text{CH}_3)_2\text{CO}$	 (57)	257
		Zn, CH_3CN , reflux	$(\text{CH}_3)_2\text{CO}$	 (52)	257
			Intramolecular	 (83)	156
		, THF, -23°	Intramolecular	 (90)	138
		, THF, -23°	Intramolecular	 (81)	138
		, THF, -23°	Intramolecular	 (98)	138
		, THF, -23°	Intramolecular	 (98)	138

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

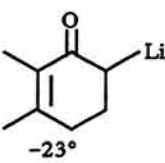
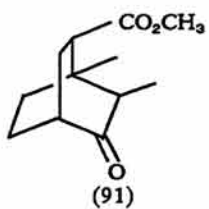
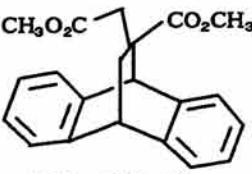
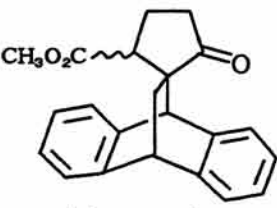
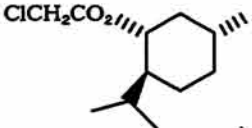
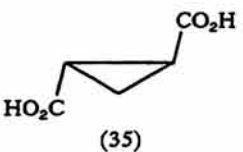
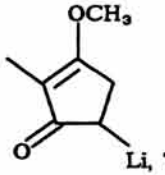
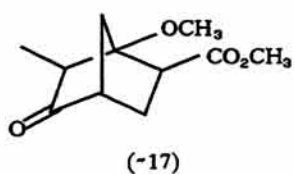
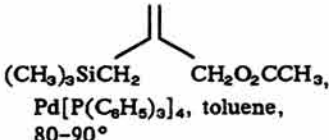
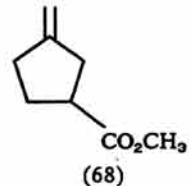
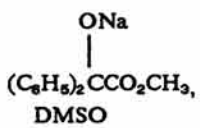
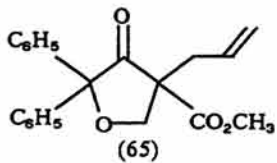
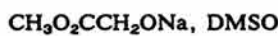
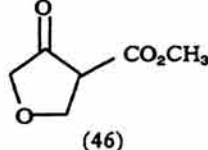
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		, THF, -23°	Intramolecular	 (91)	138
472		LDA, THF, 0°	Intramolecular, CH ₃ OH/HCl, reflux	 3:1, <i>trans:cis</i> (35)	325
		NaH, CH ₃ OH, C ₆ H ₆	KOH, HOCH ₂ CH ₂ OH	 (35)	392
		Li, THF, -78°	Intramolecular	 (-17)	393
473		(CH ₃) ₃ SiCH ₂ , Pd[P(C ₆ H ₅) ₃] ₄ , toluene, 80-90°	Intramolecular	 (68)	215
		(C ₆ H ₅) ₂ CCO ₂ CH ₃ , DMSO	CH ₂ =CHCH ₂ Br	 (65)	394
		CH ₃ O ₂ CCH ₂ ONa, DMSO	Intramolecular	 (46)	148

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

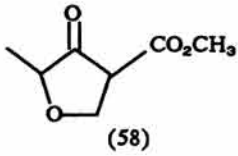
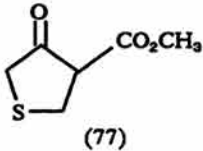
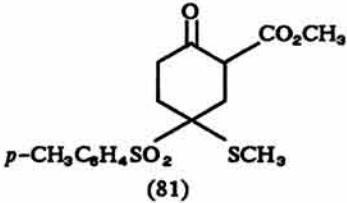
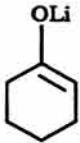
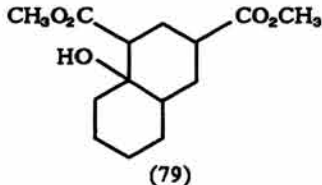
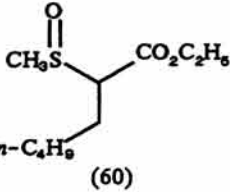
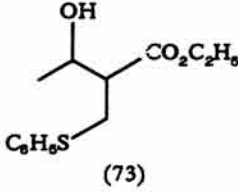
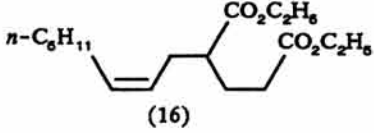
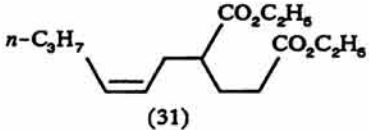
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
474		$\text{CH}_3\text{O}_2\text{CCH}(\text{CH}_3)\text{ONa}$, DMSO	Intramolecular	 (58)	148
		$\text{CH}_3\text{O}_2\text{CCH}_2\text{SNa}$, DMSO	Intramolecular	 (77)	148
		$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$ DMF	$\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$	 (81)	166
		 , THF, -78°	$\text{CH}_2=\text{CHCO}_2\text{CH}_3$	 (79)	226
	$\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$	$n\text{-C}_4\text{H}_9\text{MgBr}$, 2 mol % CuCl, -30°	CH_3SOCl , -78°	 (60)	357
475		$(\text{CH}_3)_2\text{AlSC}_6\text{H}_5$, CH_2Cl_2 , -78°	CH_3CHO , THF	 (73)	204
		$[(Z)\text{-}n\text{-C}_6\text{H}_{11}\text{CH}=\text{CH}]_2\text{CuLi}$	$\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$	 (16)	395
		$[(Z)\text{-}n\text{-C}_3\text{H}_7\text{CH}=\text{CH}]_2\text{CuLi}$	$\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$	 (31)	395

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

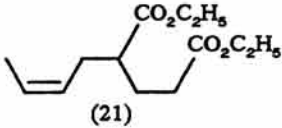
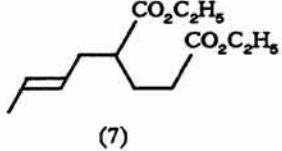
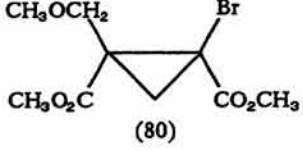
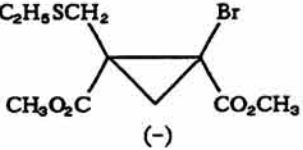
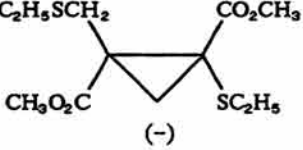
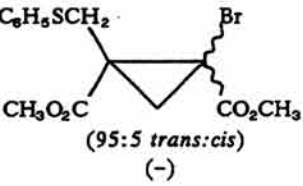
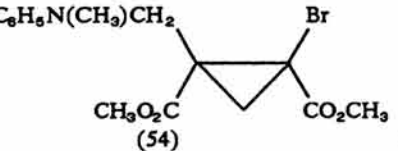
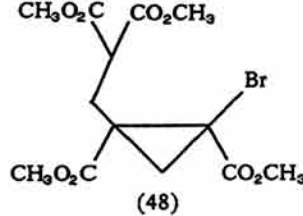
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		$[(Z)-CH_3CH=CH]_2CuLi$	$CH_2=CHCO_2C_2H_5$	 (21)	395
		$[(E)-CH_3CH=CH]_2CuLi$	$CH_2=CHCO_2C_2H_5$	 (7)	395
	$CH_2=CBrCO_2CH_3$	$CH_3OLi, 0.5 \text{ eq}, THF, -50^\circ$	Self	 (80)	141
		$C_2H_5SLi, 0.5 \text{ eq}, THF, -50^\circ$	Self	 (-)	141
		$C_2H_5SLi, 1.0 \text{ eq}, THF, -50^\circ$	Self	 (-)	141
		$C_6H_5SLi, 0.5 \text{ eq}, THF, -50^\circ$	Self	 (95:5 <i>trans:cis</i>) (-)	141
		$C_6H_5N(CH_3)Li, 0.5 \text{ eq}, THF, -50^\circ$	Self	 (54)	141
		$CH_3O_2CCHLiCO_2CH_3, 0.5 \text{ eq}, THF, -50^\circ$	Self	 (48)	141

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

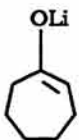
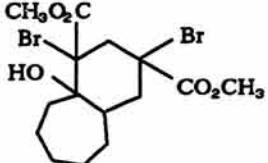
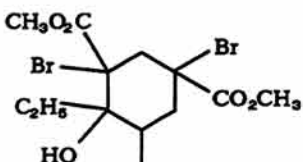
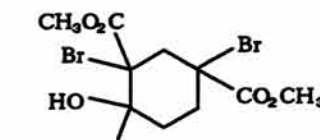
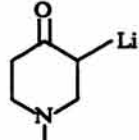
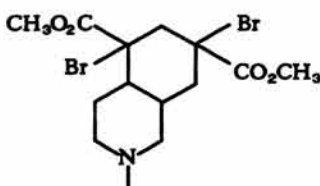
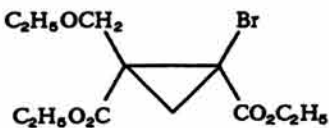
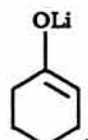
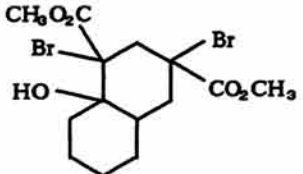
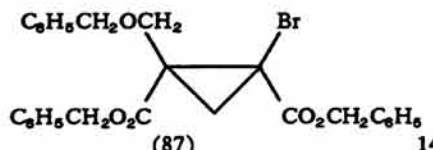
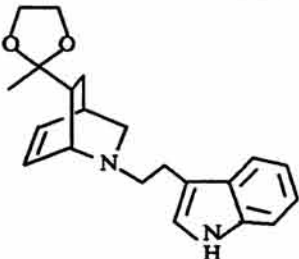
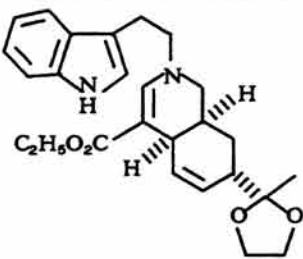
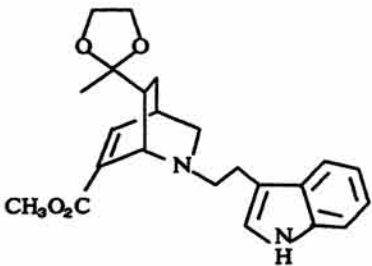
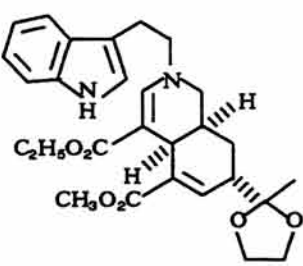
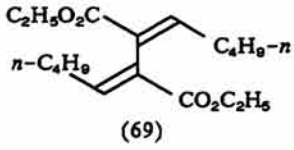
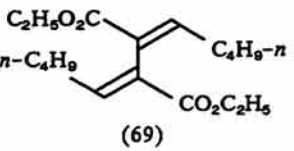
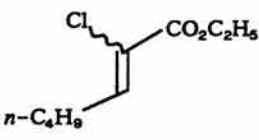
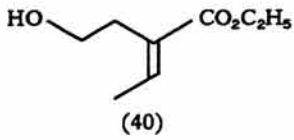
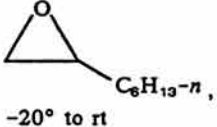
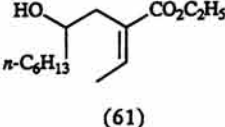
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		, THF, -78°	$\text{CH}_2=\text{CBrCO}_2\text{CH}_3$	 (73)	226
	$\text{C}_2\text{H}_5\text{COCH}_2\text{Li}$		$\text{CH}_2=\text{CBrCO}_2\text{CH}_3$	 (69)	226
	$p\text{-CH}_3\text{OC}_6\text{H}_4\text{COCH}_2\text{Li}$		$\text{CH}_2=\text{CBrCO}_2\text{CH}_3$	 (50)	226
		$\text{CH}_2\text{C}_6\text{H}_5$, THF, -78°	$\text{CH}_2=\text{CBrCO}_2\text{CH}_3$	 (66)	226
	$\text{CH}_2=\text{CBrCO}_2\text{C}_2\text{H}_5$	$\text{C}_2\text{H}_5\text{OLi}$, 0.5 eq THF, -50°	Self	 (70)	141
		, THF, -78°	Self	 (54)	226
	$\text{CH}_2=\text{CBrCO}_2\text{CH}_2\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{CH}_2\text{OLi}$, 0.5 eq THF, -50°	Self	 (87)	141

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
480	$\text{HC}\equiv\text{CCO}_2\text{C}_2\text{H}_5^a$	 CH_3CN , reflux	Intramolecular	 (60)	396
	 $\text{CH}_3\text{O}_2\text{C}$ CH_3CN , reflux	Intramolecular	 (68)	396	
	$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{C}_4\text{H}_9\text{-}n)\text{Li}$, -78°	Br_2	 (69)	249	
	$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{C}_4\text{H}_9\text{-}n)\text{Li}$, -78°	<i>N</i> -Chlorosuccinimide	 (69)	249	
			 $n\text{-C}_4\text{H}_9$ 1:1.7 (95)		
	$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{CH}_3)\text{Li}$	Ethylene oxide, -20°	 (40)	249	
	$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{CH}_3)\text{Li}$	 $\text{C}_6\text{H}_{13}\text{-}n$, -20° to rt	 (61)	249	

480

481

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

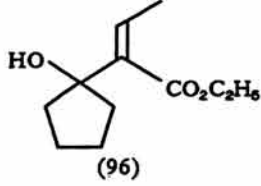
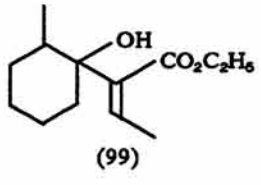
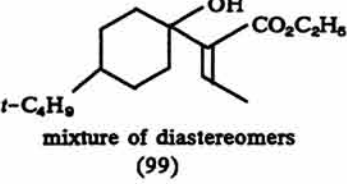
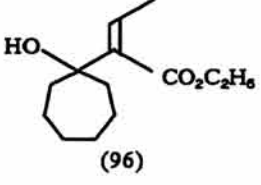
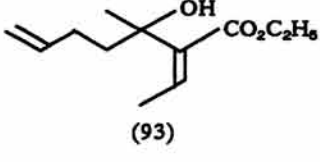
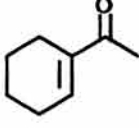
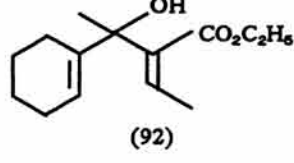
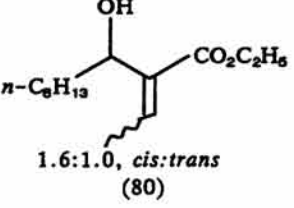
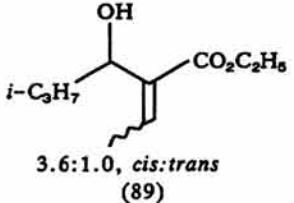
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
482		$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{CH}_3)\text{Li}$	Cyclopentanone, -78°	 (96)	249
		$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{CH}_3)\text{Li}$	2-Methylcyclohexanone, -78°	 (99)	249
		$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{CH}_3)\text{Li}$	4- <i>tert</i> -Butylcyclohexanone, -78°	 <i>t</i> -C ₄ H ₉ mixture of diastereomers (99)	249
		$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{CH}_3)\text{Li}$	Cycloheptanone	 (96)	249
		$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{CH}_3)\text{Li}$	$\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{COCH}_3$, -78°	 (93)	249
483		$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{CH}_3)\text{Li}$	 , -78°	 (92)	249
		$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{CH}_3)\text{Li}$	$n\text{-C}_9\text{H}_{19}\text{CHO}$	 $n\text{-C}_9\text{H}_{19}$ 1.6:1.0, <i>cis:trans</i> (80)	249
		$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{CH}_3)\text{Li}$	$i\text{-C}_3\text{H}_7\text{CHO}$, -78°	 $i\text{-C}_3\text{H}_7$ 3.6:1.0, <i>cis:trans</i> (89)	249

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.	
484		$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{CH}_3)\text{Li}$	$\text{C}_6\text{H}_5\text{CHO}$, -78°	 4.0:1.0, <i>cis:trans</i> (86)	249	
		$(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Cu}(\text{C}_4\text{H}_9\text{-}n)\text{Li}$	Cyclopentanone, -78°	 (98)	249	
		$\text{CH}_3\text{Cu}(\text{CN})\text{Li}$, -78°	$(E)\text{-CH}_3\text{CH=CHCOCl}$	 (75)	110	
		$\text{CH}_3\text{Cu}(\text{C}\equiv\text{CC}_4\text{H}_9\text{-}n)\text{Li}$, -78°	$(E)\text{-C}_6\text{H}_5\text{CH=CHCOCl}$	 (82)	110	
		$\text{CH}_3\text{Cu}(\text{C}\equiv\text{CC}_4\text{H}_9\text{-}n)\text{Li}$, -78°		 (87)	110	
	485		$\text{CH}_3\text{Cu}(\text{C}\equiv\text{CC}_4\text{H}_9\text{-}n)\text{Li}$, -78°		 (80)	110
			$\text{CH}_3\text{Cu}(\text{C}\equiv\text{CC}_4\text{H}_9\text{-}n)\text{Li}$, -78°		 (85)	110
			$\text{CH}_3\text{Cu}(\text{C}\equiv\text{CC}_4\text{H}_9\text{-}n)\text{Li}$, -78°		 (92)	110

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

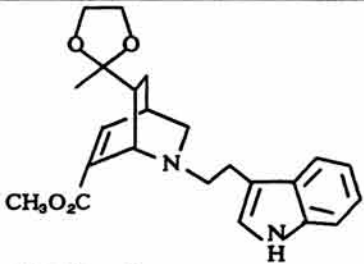
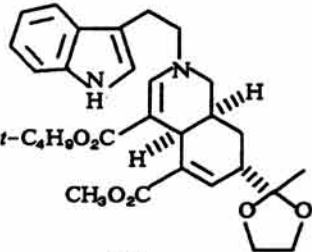
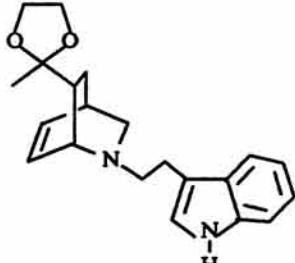
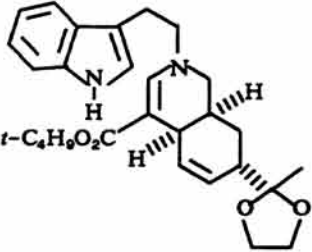
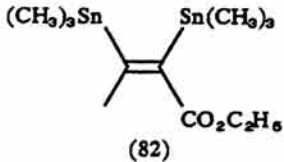
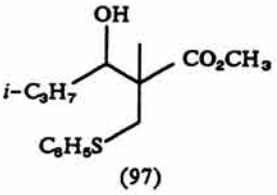
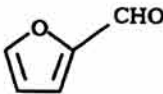
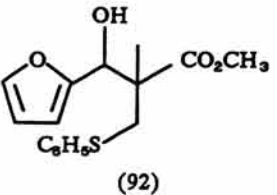
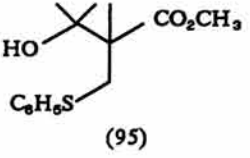
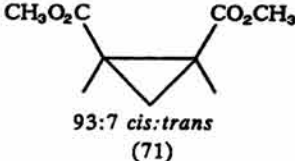
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
486	$\text{HC}\equiv\text{CCO}_2\text{C}_4\text{H}_9-t$	 CH_3CN , reflux	Intramolecular	 (23)	396
		 CH_3CN , 80° , 24 h	Intramolecular	 (65)	202
4	$\text{CH}_3\text{C}\equiv\text{CCO}_2\text{C}_2\text{H}_5$	$[(\text{CH}_3)_3\text{Sn}]_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF	-	 (82)	252
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$	$\text{C}_6\text{H}_5\text{SMgI}$, $(\text{C}_2\text{H}_5)_2\text{O}/n\text{-C}_8\text{H}_{14}$, 0°	$i\text{-C}_3\text{H}_7\text{CHO}$	 (97)	145
487		$\text{C}_6\text{H}_5\text{SMgI}$, $(\text{C}_2\text{H}_5)_2\text{O}/n\text{-C}_8\text{H}_{14}$, 0°		 (92)	145
		$\text{C}_6\text{H}_5\text{SMgI}$, $(\text{C}_2\text{H}_5)_2\text{O}/n\text{-C}_8\text{H}_{14}$, 0°	$(\text{CH}_3)_2\text{CO}$	 (95)	145
		$\text{CH}_3\text{O}_2\text{CCHClCH}_3$, NaH , Toluene	Intramolecular	 93:7 <i>cis:trans</i> (71)	279

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

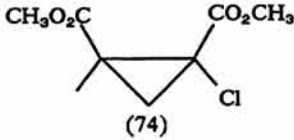
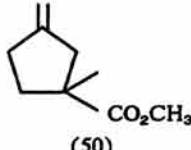

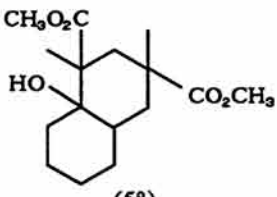
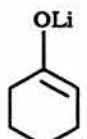
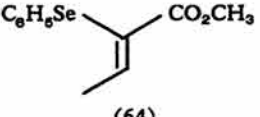
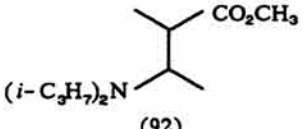
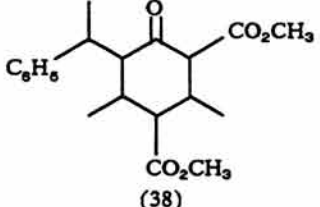
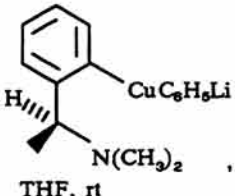
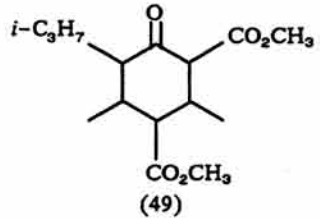
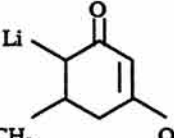
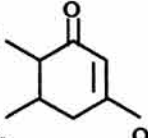
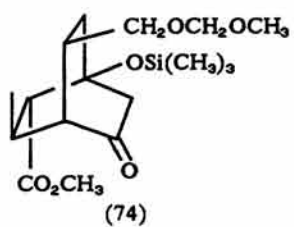
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		$\text{CH}_3\text{O}_2\text{CCHCl}_2$, NaH, Toluene	Intramolecular	 (74)	279
	 (50)	$(\text{CH}_3)_3\text{SiCH}_2$  $\text{CH}_2\text{O}_2\text{CCH}_3$, Pd[P(C ₆ H ₅) ₃] ₄ , toluene, 80-90°	Intramolecular		215
	 (58)	 , THF, -78°	Self		226
	<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHCO}_2\text{CH}_3$	LDA, THF, 0°	C ₆ H ₅ SeBr	 (64)	203
		LDA, THF, 0°	CH ₃ I	 (92)	203
	 (38)	 , THF, rt	Self		109
	 (49)	$(\text{CH}_3)_2\text{CuLi}$, THF, 10°	Self		109
		$\text{CH}_3\text{OCH}_2\text{OCH}_2$  $\text{OSi}(\text{CH}_3)_3$, THF, -78°	Intramolecular	 (74)	309

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		$(\text{CH}_3)_3\text{SiCH}_2$ Pd[P(C ₆ H ₅) ₃] ₄ , toluene, reflux	Intramolecular	 13:1, <i>trans:cis</i> (38)	215
		OC ₄ H ₉ - <i>t</i> , THF, -78°	CH ₃ I, KOC ₄ H ₉ - <i>t</i>	 $\geq 10:1$ <i>trans:cis</i> (70)	129
		OC ₄ H ₉ - <i>t</i> , THF, -78°	CH ₃ I, HMPA	" 2:1 <i>trans:cis</i> (59)	129
		LDA, -78°	Intramolecular	 (-52)	195
		CH ₃ O ₂ CCH ₂ ONa, DMSO	Intramolecular	 (65)	148
		C ₆ H ₅ SMgI, (C ₂ H ₅) ₂ O/ <i>n</i> -C ₈ H ₁₄ , 0°	<i>i</i> -C ₃ H ₇ CHO	 (90)	145
		C ₆ H ₅ SMgI, (C ₂ H ₅) ₂ O/ <i>n</i> -C ₈ H ₁₄ , 0°	<i>n</i> -C ₈ H ₁₃ CHO	 (83)	145

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

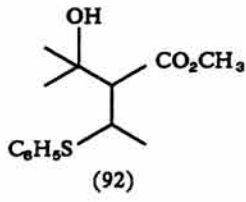
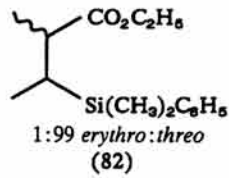
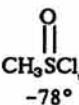
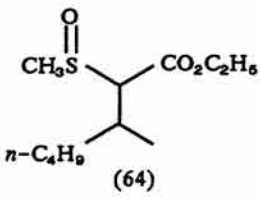
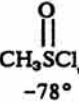
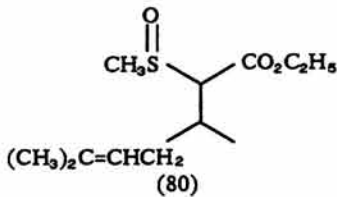
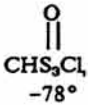
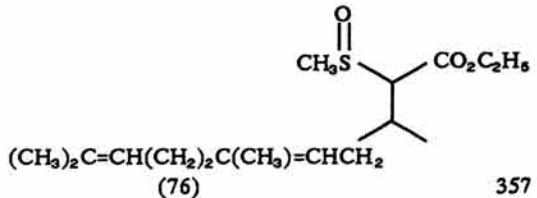
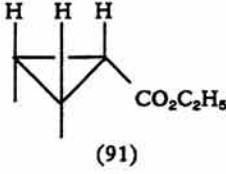
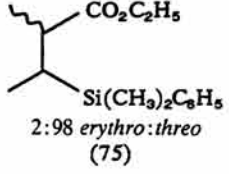
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
492		C_6H_5SMgI , $(C_2H_5)_2O/n-C_8H_{14}$, 0°	$(CH_3)_2CO$	 (92)	145
	<i>trans</i> - $CH_3CH=CHCO_2H_5$	$[C_6H_5(CH_3)_2Si]_2CuLi$	CH_3I	 1:99 <i>erythro:threo</i> (82)	102
		$n-C_4H_9MgBr$, 2 mol % $CuCl$, -30°	 -78°	 $n-C_4H_9$ (64)	357
		$(CH_3)_2C=CHCH_2MgBr$, 2 mol % $CuCl$, -30°	 -78°	 $(CH_3)_2C=CHCH_2$ (80)	357
493		$(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCH_2MgBr$, 2 mol % $CuCl$, -30°	 -78°	 $(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCH_2$ (76)	357
		$CH_3\bar{C}HP(C_6H_5)_3$	Intramolecular	 (91)	170
	<i>cis</i> - $CH_3CH=CHCO_2C_2H_5$	$[C_6H_5(CH_3)_2Si]_2CuLi$	CH_3I	 2:98 <i>erythro:threo</i> (75)	102

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

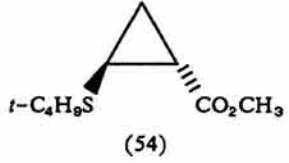
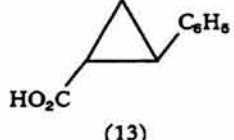
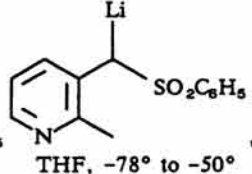
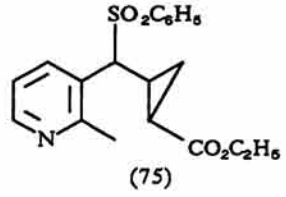
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
494	$trans\text{-BrCH}_2\text{CH=CHCO}_2\text{CH}_3$	$t\text{-C}_4\text{H}_9\text{SLi}$, THF, 0°	Intramolecular	 (54)	128
				”	
		$t\text{-C}_4\text{H}_9\text{SLi}$, CH_2Cl_2 , 0°	Intramolecular	$t\text{-C}_4\text{H}_9\text{S}$ (73)	397
		$t\text{-C}_4\text{H}_9\text{SLi}$, 0°	Intramolecular	” (70)	397
		$t\text{-C}_4\text{H}_9\text{SLi}$, THF, 0°	Intramolecular	” (65)	397
		$t\text{-C}_4\text{H}_9\text{SLi}$, C_2H_6 , 0°	Intramolecular	” (81)	397
		$t\text{-C}_4\text{H}_9\text{SLi}$, C_5H_{12} , 0°	Intramolecular	” (74)	397
		$\text{C}_6\text{H}_5\text{MgBr}$, rt	Intramolecular, saponify	 (13)	398
495	$trans\text{-BrCH}_2\text{CH=CHCO}_2\text{C}_2\text{H}_5$	 THF, -78° to -50°	Intramolecular	 (75)	276

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

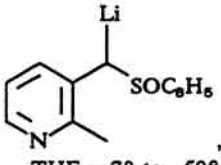
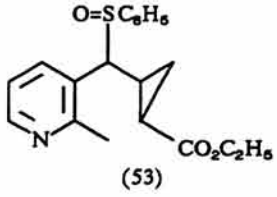
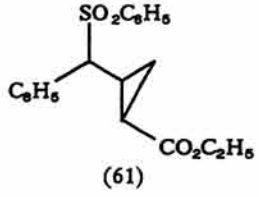
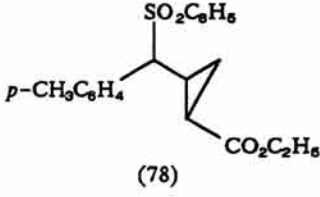
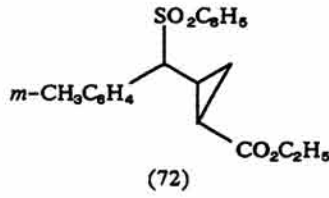
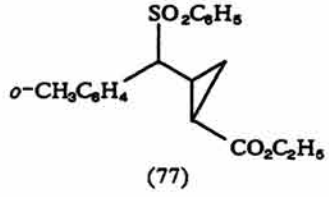
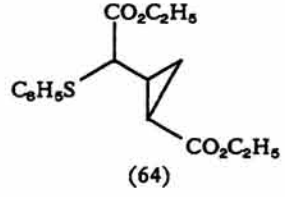
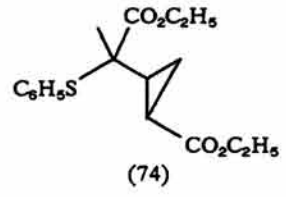
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		THF, -78 to -50°	Intramolecular	 (53)	276
		$C_6H_5CHLiSO_2C_6H_5$, THF, -65°	Intramolecular	 (61)	276
		$p-CH_3C_6H_4CHLiSO_2C_6H_5$, THF, -65°	Intramolecular	 (78)	276
		$m-CH_3C_6H_4CHLiSO_2C_6H_5$, THF, -65°	Intramolecular	 (72)	276
		$o-CH_3C_6H_4CHLiSO_2C_6H_5$, THF, -65°	Intramolecular	 (77)	276
		$C_6H_5SCHLiCO_2C_2H_5$, THF, -60°	Intramolecular	 (64)	276
		$C_6H_5SC(CH_3)LiCO_2C_2H_5$, THF, -60°	Intramolecular	 (74)	276

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		$\text{OC}_4\text{H}_9\text{-}t$, THF, -78°	$\text{KOC}_4\text{H}_9\text{-}t$	 (84)	129
		$\text{OC}_4\text{H}_9\text{-}t$, THF, -78°	$\text{KOC}_4\text{H}_9\text{-}t$	 (76)	129
		$\text{OC}_4\text{H}_9\text{-}t$, THF, -78°	$\text{KOC}_4\text{H}_9\text{-}t$, HMPA	 (89)	129
Dimethyl fumarate		$(\text{CH}_3)_3\text{SiCH}_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF, reflux	Intramolecular	 (32)	215
Dimethyl maleate		$(\text{CH}_3)_3\text{SiCH}_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF, reflux	Intramolecular	 1.3:1 <i>trans:cis</i> (60)	215
		$(\text{CH}_3)_3\text{SiCH}_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, toluene, 100°	Intramolecular	" 25:1 <i>trans:cis</i> (50)	215
$\text{CH}_3\text{O}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3$		$\text{R Cu} \bullet$ DMS, THF, MgBr_2 , $\geq -40^\circ$, $\text{R}=\text{C}_2\text{H}_5$, $n\text{-C}_4\text{H}_9$, $n\text{-C}_8\text{H}_{17}$, $n\text{-C}_8\text{H}_{13}$, $(\text{CH}_3)_2\text{C}=\text{CC}_3\text{H}_7$, $\text{CH}_2=\text{CH}$, (<i>E</i>)- $\text{CH}_3\text{CH}=\text{CH}$, $(\text{CH}_3)_3\text{Si}$, C_6H_5 , $\text{C}_6\text{H}_5\text{CH}_2$	Substrate	 (-)	93

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		 NaOCH ₃ , CH ₃ OH	Intramolecular	 (70)	146
	CH ₂ =C=CHCO ₂ C ₂ H ₅	(CH ₃) ₂ CuLi, -90°	CH ₃ I, DME, -30°	 (95)	255
		(CH ₃) ₂ CuLi, -90°	CH ₂ =CHCH ₂ Cl, DME, -30°	 (95)	255
		(CH ₃) ₂ CuLi, -90°	(CH ₃) ₂ C=CHCH ₂ Br, DME, -30°	 (95)	255
5	C ₂ H ₅ C≡CCO ₂ CH ₃	(CH ₃) ₂ CuLi	CH ₃ I	 (25)	97
	ClCH ₂ CH ₂ C≡CCO ₂ C ₂ H ₅	[(CH ₃) ₃ Sn] ₂ , Pd[P(C ₆ H ₅) ₃] ₄ , THF	-	 (90)	252
	BrCH ₂ CH ₂ C≡CCO ₂ C ₂ H ₅	[(CH ₃) ₃ Sn] ₂ , Pd[P(C ₆ H ₅) ₃] ₄ , THF	-	 (90)	252
	CH ₂ =C=C(CH ₃)CO ₂ C ₂ H ₅	(CH ₃) ₂ CuLi, -90°	CH ₃ I, DME, -30°	 (95)	255
		(CH ₃) ₂ CuLi, -90°	CH ₂ =CHCH ₂ Cl, DME, -30°	 (95)	255

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

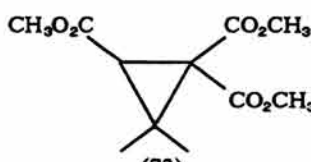
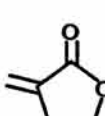
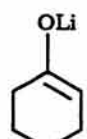
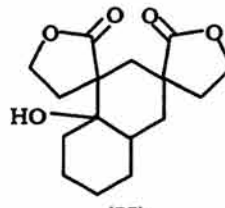
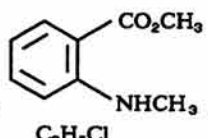
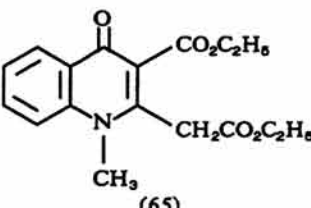
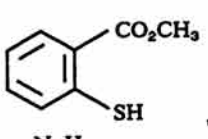
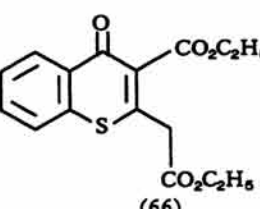
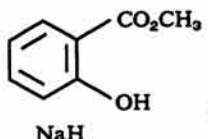
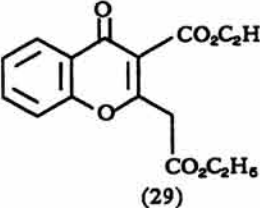
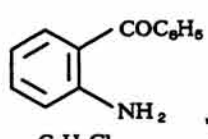
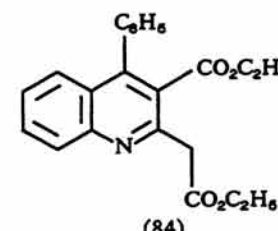
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
	$\text{CH}_3\text{O}_2\text{CCH}=\text{C}(\text{CO}_2\text{CH}_3)_2$	$\text{O}_2\text{NC}(\text{CH}_3)_2\text{K}$, THF, 20°	DMSO, 60° ; H_2O	 (72)	178
502		 , THF, -78°	Self	 (77)	226
	$\text{C}_2\text{H}_5\text{O}_2\text{CCH}=\text{C}=\text{CHCO}_2\text{C}_2\text{H}_5$	 $\text{C}_6\text{H}_5\text{Cl}$	$t\text{-C}_4\text{H}_9\text{OK}$, intramolecular	 (65)	149
		 NaH , THF,	Intramolecular	 (66)	149
		 NaH , THF,	Intramolecular	 (29)	149
503		 $\text{C}_6\text{H}_5\text{Cl}$, THF,	$t\text{-C}_4\text{H}_9\text{OK}$, intramolecular	 (84)	149

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

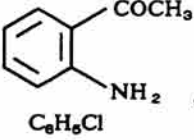
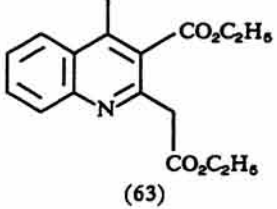
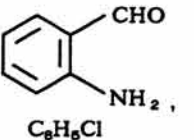
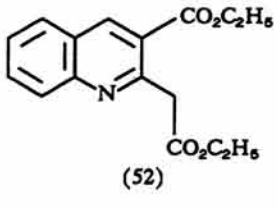
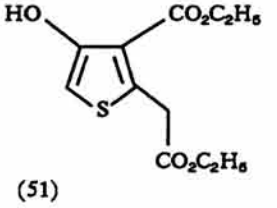
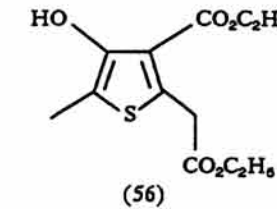
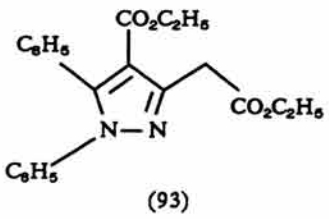
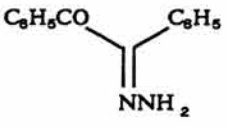
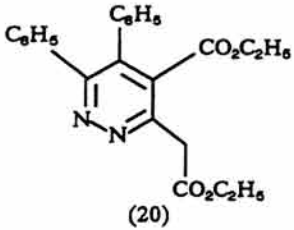
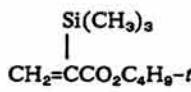
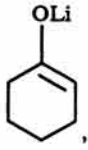
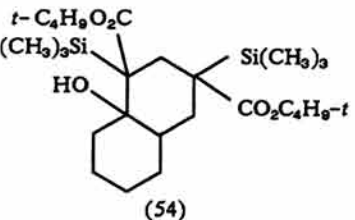
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		$\text{C}_6\text{H}_5\text{Cl}$	$t\text{-C}_4\text{H}_9\text{OK}$, intramolecular		149
		$\text{C}_6\text{H}_5\text{Cl}$	$t\text{-C}_4\text{H}_9\text{OK}$, intramolecular		149
	$\text{HSCH}_2\text{CO}_2\text{CH}_3$, $\text{C}_6\text{H}_5\text{Cl}$		$t\text{-C}_4\text{H}_9\text{OK}$, intramolecular		149
	$\text{HSCH}(\text{CH}_3)\text{CO}_2\text{CH}_3$, $\text{C}_6\text{H}_5\text{Cl}$		$t\text{-C}_4\text{H}_9\text{OK}$, intramolecular		149
	$\text{H}_2\text{NN}(\text{C}_6\text{H}_5)\text{COC}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{Cl}$		$t\text{-C}_4\text{H}_9\text{OK}$, intramolecular		149
		$\text{C}_6\text{H}_5\text{Cl}$	$t\text{-C}_4\text{H}_9\text{OK}$, intramolecular		149
6 ^a			THF, -78°	$t\text{-C}_4\text{H}_9\text{O}_2\text{C}$ 	226

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

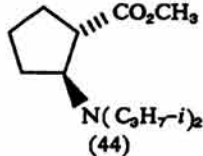
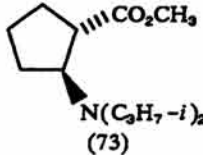
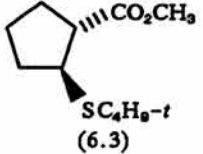
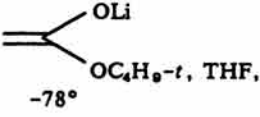
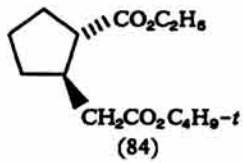
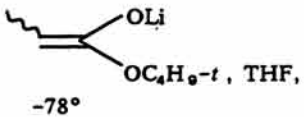
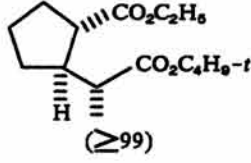
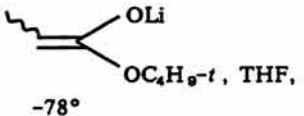
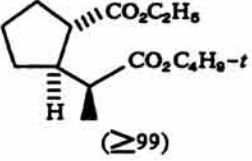
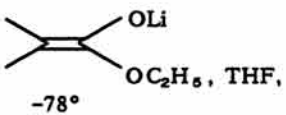
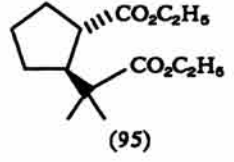
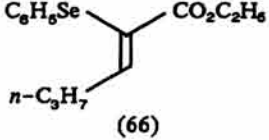
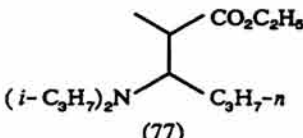
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
	$(E)\text{-Cl(CH}_2)_3\text{CH=CHCO}_2\text{CH}_3$	LDA, THF, -78°	Intramolecular	 N(C ₃ H ₇ -i) ₂ (44)	128
506	$(E)\text{-Br(CH}_2)_3\text{CH=CHCO}_2\text{CH}_3$	LDA, THF, -78°	Intramolecular	 N(C ₃ H ₇ -i) ₂ (73)	128
		<i>t</i> -C ₄ H ₉ SLi, THF, rt	Intramolecular	 SC ₄ H ₉ - <i>t</i> (6.3)	128
	$(E)\text{-I(CH}_2)_3\text{CH=CHCO}_2\text{C}_2\text{H}_5$	 -78°	KOC ₄ H ₉ - <i>t</i>	 CH ₂ CO ₂ C ₄ H ₉ - <i>t</i> (84)	129
		 -78°	KOC ₄ H ₉ - <i>t</i>	 H (≥99)	129
		 -78°	KOC ₄ H ₉ - <i>t</i> , HMPA	 H (≥99)	129
507		 -78°	KOC ₄ H ₉ - <i>t</i>	 (95)	129
	$(E)\text{-}n\text{-C}_3\text{H}_7\text{CH=CHCO}_2\text{C}_2\text{H}_5$	LDA, THF, 0°	C ₆ H ₅ SeBr	 n-C ₃ H ₇ (66)	203
		LDA, THF, 0°	CH ₃ I	 (<i>i</i> -C ₃ H ₇) ₂ N (77)	203

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

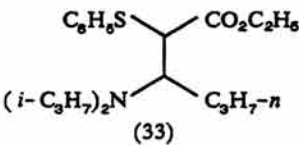
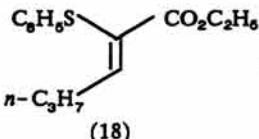
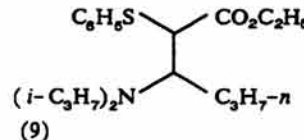
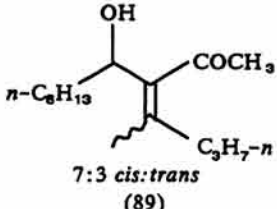
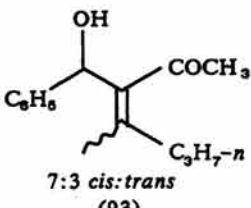
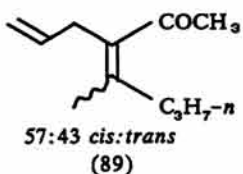
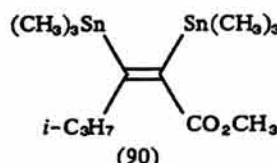

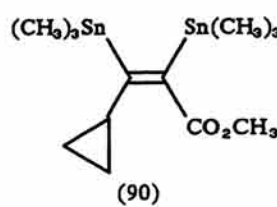
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		LDA, THF, 0°	(C ₆ H ₆) ₂ S ₂	 (33)	203
		LDA, THF, 0°	C ₆ H ₅ SCl	 (18)	203
				 (9)	
	<i>n</i> -C ₃ H ₇ C≡CCO ₂ CH ₃	(<i>n</i> -C ₄ H ₉ C≡C)Cu(CH ₃)Li	<i>n</i> -C ₈ H ₁₃ CHO	 7:3 <i>cis:trans</i> (89)	249
		(<i>n</i> -C ₄ H ₉ C≡C)Cu(CH ₃)Li	C ₆ H ₅ CHO	 7:3 <i>cis:trans</i> (93)	249
		(<i>n</i> -C ₄ H ₉ C≡C)Cu(CH ₃)Li	CH ₂ =CH ₂ Br	 57:43 <i>cis:trans</i> (89)	249
	<i>i</i> -C ₃ H ₇ C≡CCO ₂ CH ₃	[(CH ₃) ₃ Sn] ₂ , Pd[P(C ₆ H ₅) ₃] ₄ , THF	-	 (90)	252
	 C≡CCO ₂ CH ₃	[(CH ₃) ₃ Sn] ₂ , Pd[P(C ₆ H ₅) ₃] ₄ , THF	-	 (90)	252

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

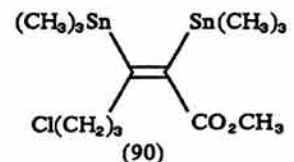
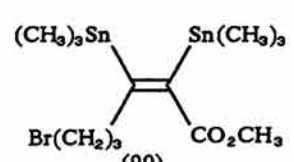
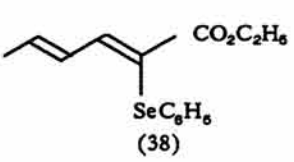
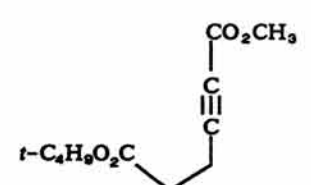
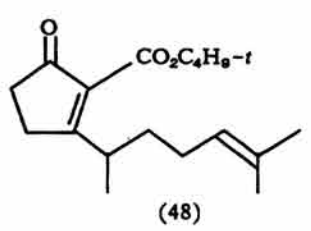
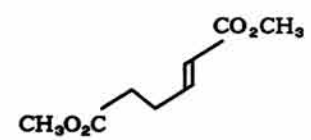
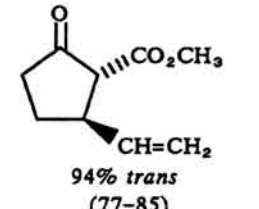
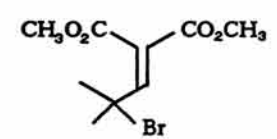
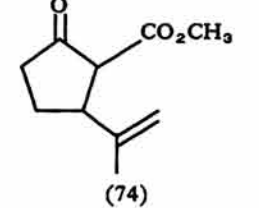
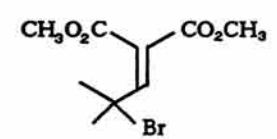
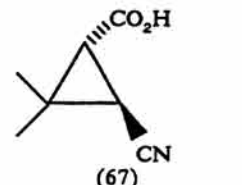
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
510	$\text{Cl}(\text{CH}_2)_3\text{C}\equiv\text{CCO}_2\text{CH}_3$	$[(\text{CH}_3)_3\text{Sn}]_2, \text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4, \text{THF}$	-	 (90)	252
	$\text{Br}(\text{CH}_2)_3\text{C}\equiv\text{CCO}_2\text{CH}_3$	$[(\text{CH}_3)_3\text{Sn}]_2, \text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4, \text{THF}$	-	 (90)	252
	$(E,E)\text{-CH}_3(\text{CH}=\text{CH})_2\text{CO}_2\text{C}_2\text{H}_5$	LDA, THF, 0°	$\text{C}_6\text{H}_6\text{SeBr}$	 (38)	203
		$(\text{CH}_2=\text{CH})_2\text{CuMgCl}, \text{THF}, -78^\circ$	Intramolecular	 (48)	99
		$(\text{CH}_2=\text{CH})_2\text{Cu}(\text{CN})\text{Li}_2, -30^\circ$	Intramolecular	 94% <i>trans</i> (77-85)	87
511		$[\text{CH}_2=\text{C}(\text{CH}_3)]_2\text{Cu}(\text{CN})\text{Li}_2, -30^\circ$	Intramolecular	 (74)	87
		NaCN, DMSO	Intramolecular	 (67)	181

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
7 ^a		$(C_2H_5O_2C)_2CHNa$, 2/1 THF/NMP, 25°	CH_3I	 (85)	228
		$(C_2H_5O_2C)_2CHNa$, 2/1 THF/NMP, 45° to 50°, 72 h	C_2H_5I	 (54)	228
		$(C_2H_5O_2C)_2CHNa$, 2/1 THF/NMP, 45° to 50°, 72 h	$n-C_3H_7I$	 (40)	228
		$(C_2H_5O_2C)_2CNa(COCH_3)$, 2/1 THF/NMP, 25°	CH_3I	 (43)	228
		$(C_2H_5O_2C)_2CNa(COCH_3)$, 2/1 THF/NMP, 25°	C_2H_5I	 (42)	228
		$(C_2H_5O_2C)_2CNa(CN)$, 2/1 THF/NMP, 25°	CH_3I	 (43)	228
			CH_3I	 (46)	228
		4/3/2 THF/NMP/HMPA, 25°			
		$C_6H_5C\equiv CLi$, $ZnCl_2$, THF, -70°	C_6H_5CHO , reflux	 3:1 E:Z (73)	165

512

513

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

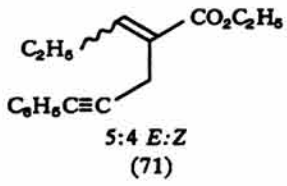
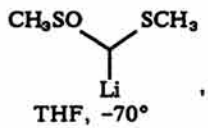
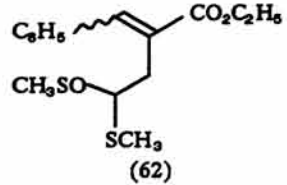
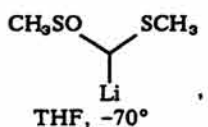
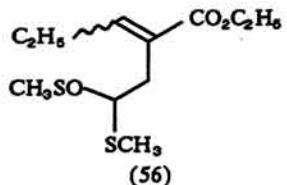
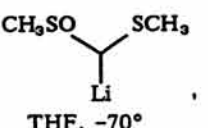
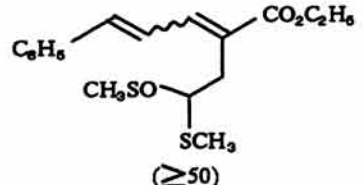
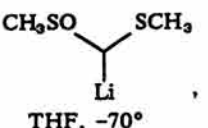
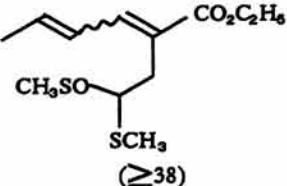
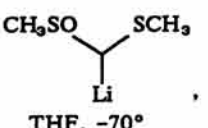
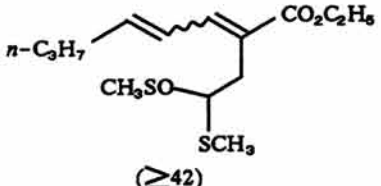
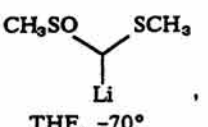
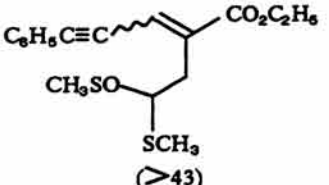
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		$C_6H_5C\equiv CLi$, $ZnCl_2$, THF, -70°	C_2H_5CHO , reflux	 $C_6H_5C\equiv C$ 5:4 E:Z (71)	165
		 THF, -70°	C_6H_5CHO , rt	 (62)	165
		 THF, -70°	C_2H_5CHO , rt	 (56)	165
		 THF, -70°	(E)- $C_6H_5CH=CHCHO$, reflux	 (≥ 50)	165
		 THF, -70°	(E)- $CH_3CH=CHCHO$, reflux	 (≥ 38)	165
		 THF, -70°	(E)- $C_3H_7CH=CHCHO$, reflux	 (≥ 42)	165
		 THF, -70°	$C_6H_5C\equiv CCHO$, reflux	 (≥ 43)	165

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		THF, -70°			165
		THF, -78°	(Z)-C ₆ H ₅ CH=CHCHO, rt		165
		THF, -78°	(E)-C ₃ H ₇ CH=CHCHO, rt		165
		THF, -78°	C ₆ H ₅ C≡CCHO, rt		165
	(E)- <i>n</i> -C ₄ H ₉ CH=CHCO ₂ CH ₃	(C ₆ H ₅) ₃ P ⁺ Li(CH ₃) ₂ , THF, rt	Intramolecular		173
	(E)- <i>i</i> -C ₄ H ₉ CH=CHCO ₂ C ₂ H ₅	LDA, THF, 0°	C ₆ H ₅ SeBr		203
	(E)-Br(CH ₂) ₄ CH=CHCO ₂ CH ₃	LDA, THF, -78°	Intramolecular		128

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

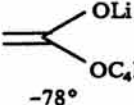
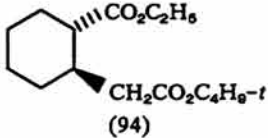
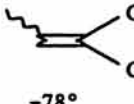
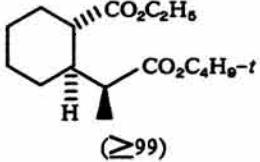
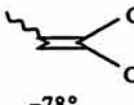
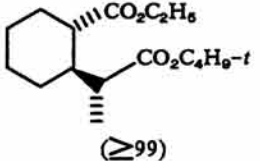
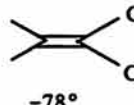
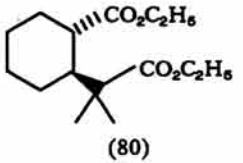
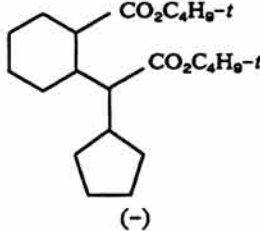
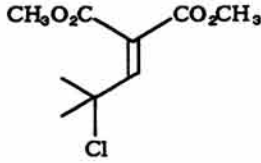
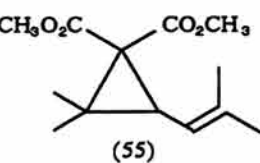
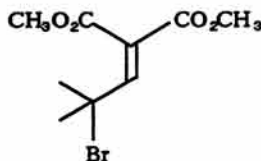
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
	(E) -I(CH ₂) ₄ CH=CHCO ₂ C ₂ H ₅	 OC ₄ H ₉ - <i>t</i> , THF, -78°	KOC ₄ H ₉ - <i>t</i>	 (94)	129
518		 OC ₄ H ₉ - <i>t</i> , THF, -78°	KOC ₄ H ₉ - <i>t</i> , HMPA	 (≥99)	129
		 OC ₄ H ₉ - <i>t</i> , THF, -78°	KOC ₄ H ₉ - <i>t</i>	 (≥99)	129
		 OC ₂ H ₅ , THF, -78°	KOC ₄ H ₉ - <i>t</i>	 (80)	129
	(E) -I(CH ₂) ₄ CH=CHCO ₂ C ₄ H ₉ - <i>t</i>	<i>n</i> -C ₄ H ₉ Li, -8°	Intramolecular	 (-)	399
519		(CH ₃) ₂ C=CHMgBr, THF, 45°	Intramolecular	 (55)	80
		(CH ₃) ₂ C=CHMgBr, cat. CuCl, 45°	Intramolecular	" (51)	80
		(CH ₃) ₂ C=CHMgBr, THF, 24°	Intramolecular	" (32)	80

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
				"	
		$(\text{CH}_3)_2\text{C}=\text{CHMgBr}$, cat. CuCl , THF, 24°	Intramolecular	(25)	80
		$(\text{CH}_3)_2\text{CuLi}$, 0°	CH_3I , 0°	$(E)\text{-C}_2\text{H}_5\text{CH}=\text{CHCH}_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{CH}_3$ (70)	227
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, 0°	$(E)\text{-C}_2\text{H}_5\text{CH}=\text{CHCH}_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{CH}_2\text{CH}=\text{CH}_2$ (75)	227
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, 0°	$(E)\text{-C}_2\text{H}_5\text{CH}=\text{CHCH}_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{CH}_2\text{C}_2\text{H}_5$ (88)	227
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, -20°	CH_3I , rt	$(E)\text{-}n\text{-C}_6\text{H}_{11}\text{CH}=\text{CHCH}_2(\text{CO}_2\text{C}_2\text{H}_5)_2\text{CH}_3$ (75)	227
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, -20°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, rt	$(E)\text{-}n\text{-C}_6\text{H}_{11}\text{CH}=\text{CHCH}_2(\text{CO}_2\text{C}_2\text{H}_5)_2\text{CH}_2\text{CH}=\text{CH}_2$ (88)	227
		$(\text{CH}_3)_2\text{CuLi}$, 0°	CH_3I , 0°	(93)	227
		$(\text{CH}_3)_2\text{CuLi}$, 0°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, 0°		227
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, -20°	CH_3I , rt		227
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, -20°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, rt		227
	$\text{Br}(\text{CH}_2)_4\text{C}\equiv\text{CCO}_2\text{CH}_3$	$[(\text{CH}_3)_3\text{Sn}]_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF	-		252

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
8 ^a		$(C_2H_5O_2C)_2CNa(COCH_3)$, 1/2/1 THF/NMP/HMPA, 40°	CH ₃ I		228
		$(C_2H_5O_2C)_2CNa(CN)$, 2/1 THF/NMP, 40°	CH ₃ I		228
	$(E)-n-C_6H_{11}CH=CHCO_2CH_3$	$(C_6H_5)_3P^+Li(CH_3)_2$, THF, rt	Intramolecular		173
	$(E)-Br(CH_2)_6CH=CHCO_2CH_3$	LDA, THF, reflux	Intramolecular		128
	$(E)-I(CH_2)_6CH=CHCO_2C_2H_5$	 -78°	KOC ₄ H _{9-t}	 1:1 mixture of epimers (60)	129
		 -78°	KOC ₄ H _{9-t}	 3.5:1 <i>trans:cis</i> (58)	129
		<i>i</i> -C ₃ H ₇ NO ₂ , K ₂ CO ₃ , C ₂ H ₅ OH, reflux	Intramolecular		177
		1) (CH ₃) ₂ CuLi, -80° 2) CH ₃ Li, -80°	I ₂	 68:32 <i>cis:trans</i> (70)	250

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

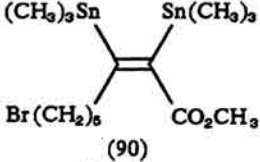
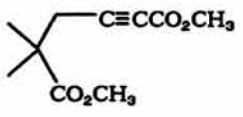
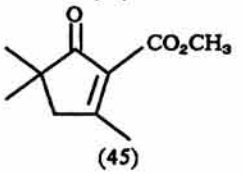
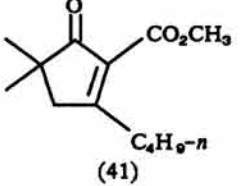
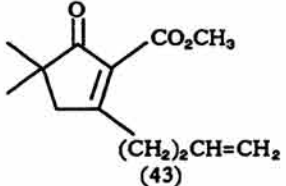
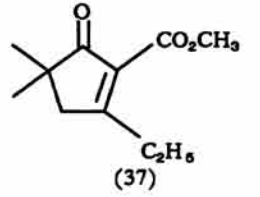
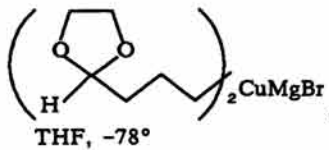
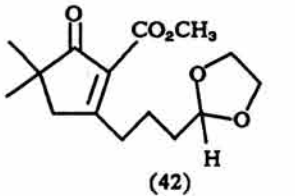
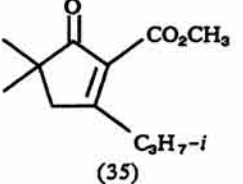
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
				”	
		CH_3MgBr , cat. CuI , -80°	I_2	37:63 <i>cis:trans</i> (-)	250
524	$\text{Br}(\text{CH}_2)_6\text{C}\equiv\text{CCO}_2\text{CH}_3$	$[(\text{CH}_3)_3\text{Sn}]_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF	-	 (90)	252
		$(\text{CH}_3)_2\text{CuLi}$, THF, -78°	Intramolecular	 (45)	99
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, THF, -78°	Intramolecular	 (41)	99
		$[\text{CH}_2=\text{CH}(\text{CH}_2)_2]_2\text{CuMgBr}$, THF, -78°	Intramolecular	 (43)	99
		$(\text{C}_2\text{H}_5)_2\text{CuMgBr}$, THF, -78°	Intramolecular	 (37)	99
525		$(\text{H})_2\text{CuMgBr}$, THF, -78°	Intramolecular	 (42)	99
		$(i\text{-C}_3\text{H}_7)_2\text{CuMgCl}$, THF, -78°	Intramolecular	 (35)	99

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

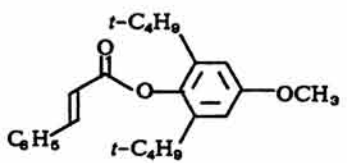
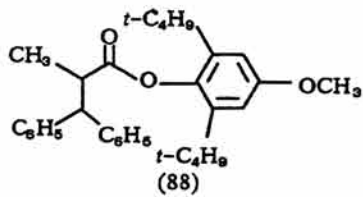
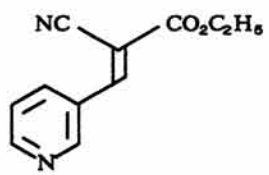
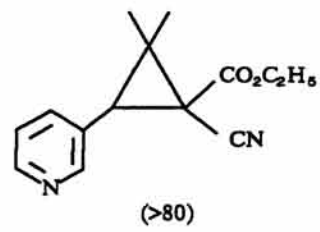
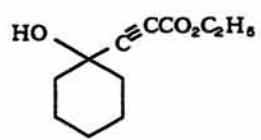
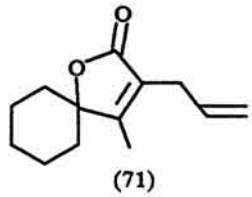
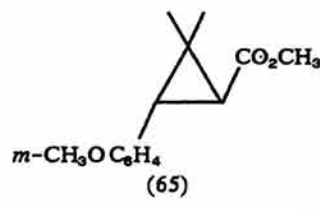
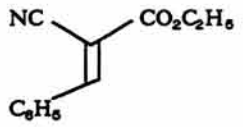
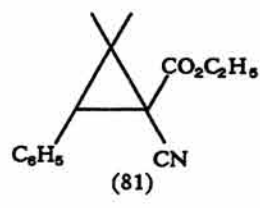
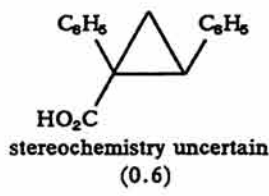
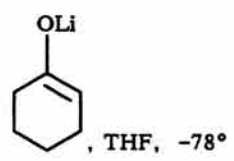
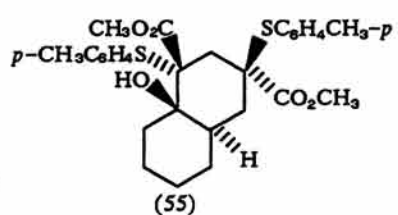
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
		$\text{C}_6\text{H}_5\text{Li}, -78^\circ$	CH_3I	 (88)	196
528		$i\text{-C}_3\text{H}_7\text{NO}_2, \text{K}_2\text{CO}_3, \text{C}_2\text{H}_5\text{OH}, \text{reflux}$	Intramolecular	 (>80)	177
		$(\text{CH}_3)_2\text{CuLi}, \text{DMS}, -78^\circ$	$\text{CH}_2=\text{CHCH}_2\text{Br}, \text{HMPA}$	 (71)	254
10	$(E)\text{-}m\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{CHCO}_2\text{CH}_3$	$(\text{C}_6\text{H}_5)_3\text{P}^+\text{Li}(\text{CH}_3)_2, \text{THF}, \text{rt}$	Intramolecular	 (65)	173
		$i\text{-C}_3\text{H}_7\text{NO}_2, \text{K}_2\text{CO}_3, \text{C}_2\text{H}_5\text{OH}, \text{reflux}$	Intramolecular	 (81)	177
529	$(E)\text{-BrCH}_2\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{CO}_2\text{CH}_3$	$\text{C}_6\text{H}_5\text{MgBr}, \text{rt}$	Intramolecular, saponify	 stereochemistry uncertain (0.6)	398
		$\text{THF}, -78^\circ$	$\text{CH}_2=\text{C}(p\text{-CH}_3\text{C}_6\text{H}_4\text{S})\text{CO}_2\text{CH}_3$	 (55)	226

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
			Intramolecular		319
530	$n\text{-C}_7\text{H}_{15}\text{C}\equiv\text{CCO}_2\text{CH}_3$	$(\text{CH}_3)_2\text{CuLi}$, THF, -78°	O_2		96
		$(\text{CH}_3)_2\text{CuLi}$, 1 eq THF, -78°	O_2		96
		$(\text{CH}_3)_2\text{CuLi}$, 1 eq THF, -78°	I_2		96
	$t\text{-C}_4\text{H}_9(\text{CH}_3)_2\text{SiOCH}_2\text{C}\equiv\text{CCO}_2\text{C}_2\text{H}_5$	$[(\text{CH}_3)_3\text{Sn}]_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF	-		252
		$[(\text{CH}_3)_3\text{Sn}]_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF	-		252
531		$[(\text{CH}_3)_3\text{Sn}]_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF	-		252
	$\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{CO}_2\text{CH}_3)_2$	$(\text{CH}_3)_3\text{SiCH}_2$ $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, toluene, $85\text{--}95^\circ$	Intramolecular		215

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
532		$\text{CH}_3\text{O}_2\text{C}-\text{CH}=\text{CH}-\text{SH}$, triton B, C_6H_6	Intramolecular	 (60)	146
11	$\text{THPO}(\text{CH}_2)_3\text{C}\equiv\text{CCO}_2\text{CH}_3$	$[(\text{CH}_3)_3\text{Sn}]_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF	-	 (90)	252
12	$(E)-m\text{-CH}_3\text{OC}_6\text{H}_4(\text{CH}_2)_2\text{CH}=\text{CHCO}_2\text{CH}_3$	$(\text{C}_6\text{H}_5)_3\text{P}^+\text{Li}(\text{CH}_3)_2$, THF, rt	Intramolecular	 (70)	173
		$(\text{CH}_3)_2\text{CuLi}$, THF, -78°	$\text{CH}_2=\text{CHBr}$, I_2 , reflux	 (85)	253
		$\text{CH}_2=\text{C}(\text{CH}_3)\text{MgBr}$, CuI , THF, -50°	Intramolecular	 (84) 4:3	306
13	$t\text{-C}_4\text{H}_9(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_4\text{C}\equiv\text{CCO}_2\text{C}_2\text{H}_5$	$[(\text{CH}_3)_3\text{Sn}]_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF	-	 (90)	252

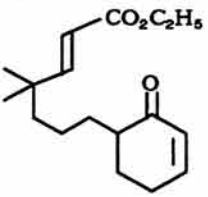
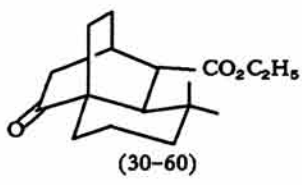
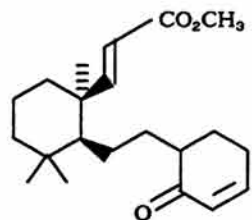
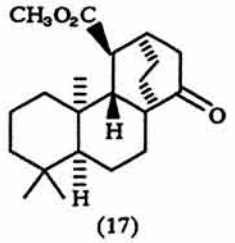
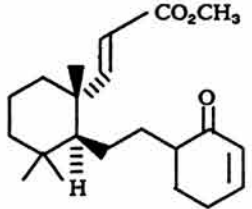
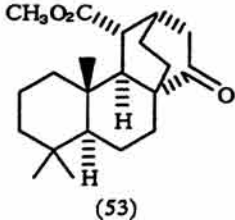
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TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
534		LHMDS, hexane	Intramolecular	 (50)	401
14		$(\text{CH}_3)_2\text{CuLi}$, THF, -78°	I_2	 (72)	253
		$(\text{CH}_3)_2\text{CuLi}$, THF, -78°	1) CH_3COCl , HMPA 2) I_2 , reflux	 (72)	253
		$(\text{CH}_3)_2\text{CuLi}$, THF, -78°	1) $\text{C}_2\text{H}_5\text{OCH}_2\text{Cl}$, HMPA 2) I_2 , reflux	 (62)	253
		$(\text{CH}_3)_2\text{CuLi}$, THF, -78°	1) $(\text{CH}_3)_2\text{S}_2$, HMPA 2) I_2 , reflux	 (62)	253
535		$(\text{CH}_3)_2\text{CuLi}$, THF, -78°	CH_3I , HMPA	 (58)	253
		$(\text{CH}_3)_2\text{CuLi}$, THF, -78°	I_2	 (51)	253

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
536 15		LHMDS, THF, -78° to rt	Intramolecular	 (30-60)	402 401
		LHMDS, THF/HMPA, -78° to rt	Intramolecular	" (10)	402
		LDA, THF, -78°	Intramolecular	" (22)	402
		LDA, THF, -78° to -20°	Intramolecular	" (45)	402
20		LHMDS, 8:1 hexane:(C ₂ H ₅) ₂ O, -78° to rt	Intramolecular	 (17)	402
537		LHMDS	Intramolecular	 (53)	140

^a See addendum to Table IIA for additional entries.

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

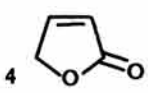
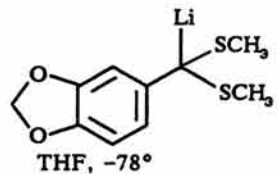
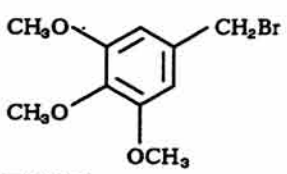
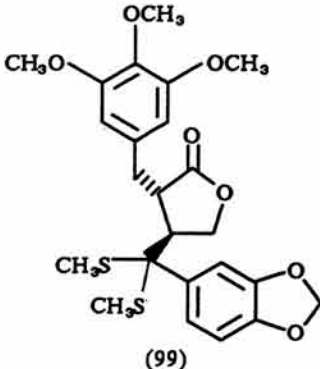
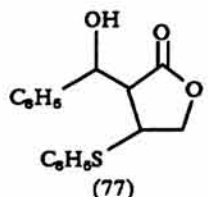
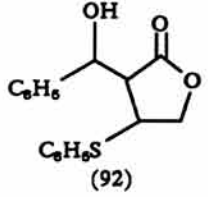
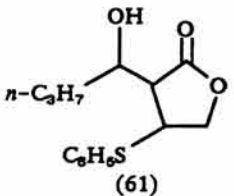
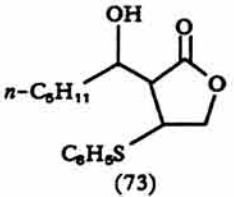
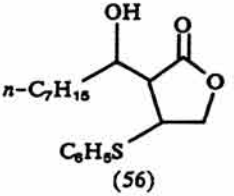
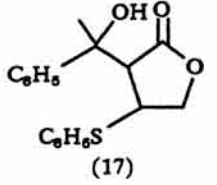
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Lactones					
4		 THF, -78°	 TMEDA	 (99)	162
		$(\text{CH}_3)_2\text{AlSC}_6\text{H}_5\text{Li}^+$, CH_2Cl_2 , -78°	$\text{C}_6\text{H}_5\text{CHO}$, THF	 (77)	204
		$\text{C}_6\text{H}_5\text{SLi}$, THF, -50°	$\text{C}_6\text{H}_5\text{CHO}$	 (92)	403
		$\text{C}_6\text{H}_5\text{SLi}$, THF, -50°	$n\text{-C}_3\text{H}_7\text{CHO}$	 (61)	403
		$\text{C}_6\text{H}_5\text{SLi}$, THF, -50°	$n\text{-C}_9\text{H}_{11}\text{CHO}$	 (73)	403
		$\text{C}_6\text{H}_5\text{SLi}$, THF, -50°	$n\text{-C}_7\text{H}_{15}\text{CHO}$	 (56)	403
		$\text{C}_6\text{H}_5\text{SLi}$, THF, -50°	$\text{C}_6\text{H}_5\text{COCH}_3$	 (17)	403

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

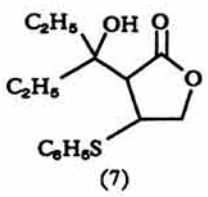
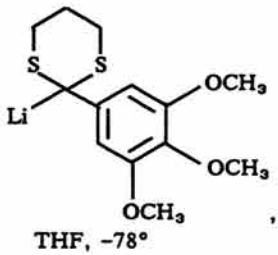
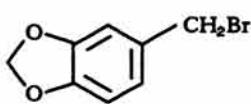
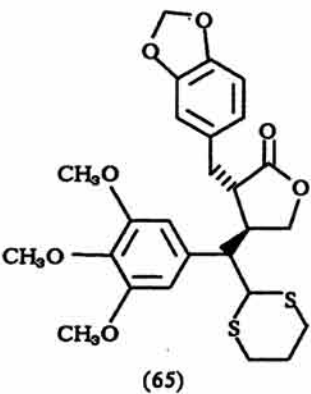
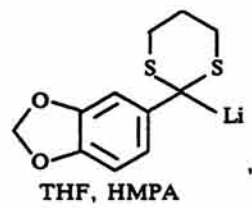
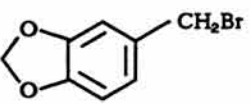
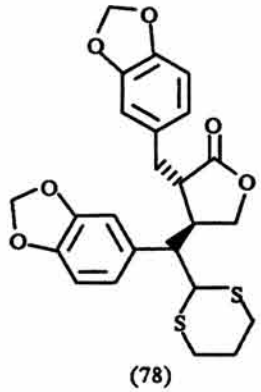
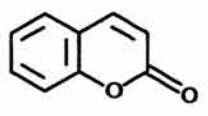
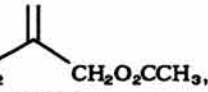
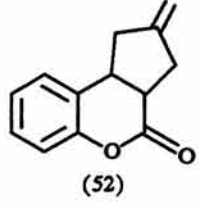
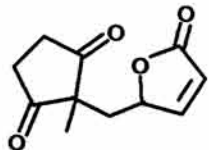
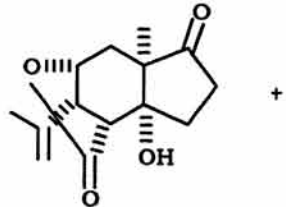
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Lactones					
		C_6H_5SLi , THF, -50°	$(C_2H_5)_2CO$	 (7)	403
	 THF, -78°			 (65)	159
	 THF, HMPA			 (78)	160
9		$(CH_3)_2SiCH_2$  $CH_2O_2CCH_3$, $Pd[P(C_6H_5)_3]$ Toluene, 115°	Intramolecular	 (52)	215
11		$CH_2=C(CH_3)MgBr$, CuI , THF, -50°	Intramolecular	 +	306

TABLE II. α,β -UNSATURATED ESTERS AND LACTONES (Continued)

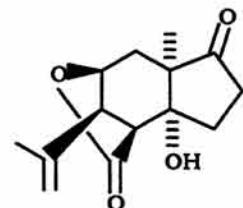
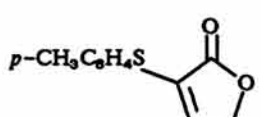
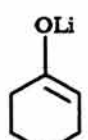
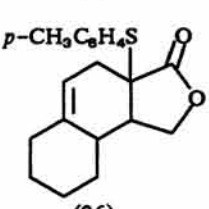
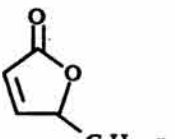
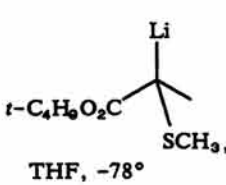
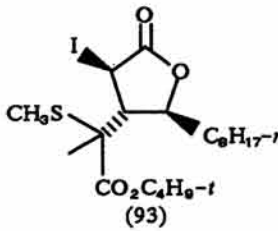
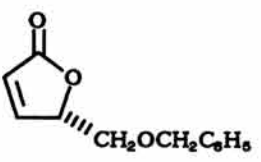
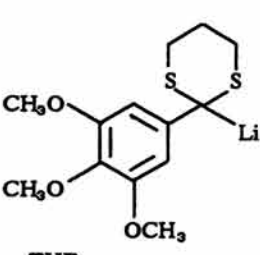
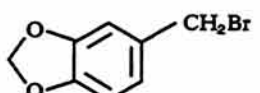
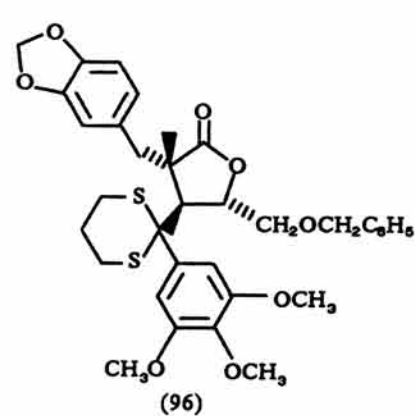
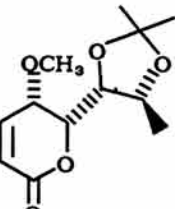
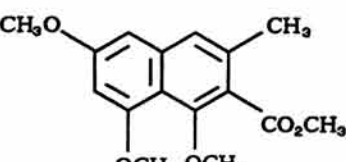
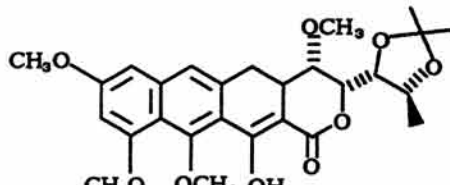
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Lactones					
				 8:1 (95)	
			$\text{CH}_2=\text{CHP}^+(\text{C}_6\text{H}_5)_3\text{Br}^-$	 (26)	143
12		 THF, -78°	I_2, THF	 (93)	303
		 THF		 (96)	163
		 LDA, THF, <i>N,N'</i> -dimethylpropyleneurea	Intramolecular	 (~51)	195

TABLE III. α,β -UNSATURATED AMIDES AND THIOAMIDES

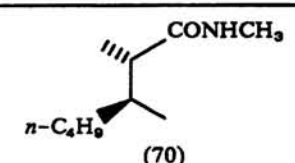
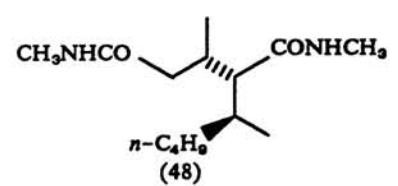
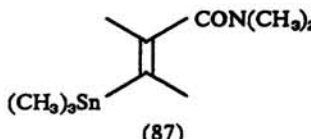
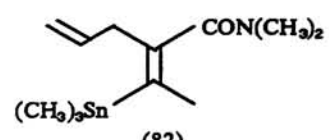
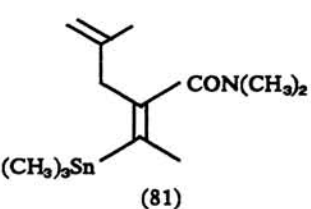
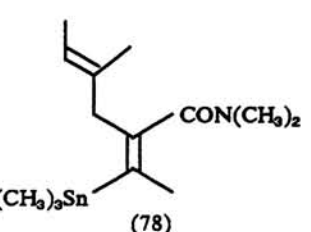
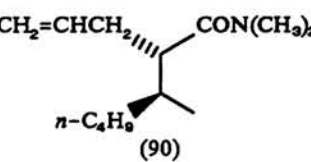
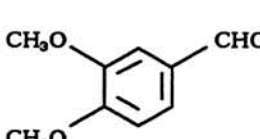
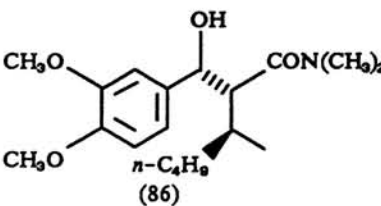
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Amides					
5	<i>trans</i> -CH ₃ CH=CHCONHCH ₃	<i>n</i> -C ₄ H ₉ Li, THF, -20° to rt	CH ₃ I	 (70)	190
		<i>n</i> -C ₄ H ₉ Li, THF, -20° to rt	Self	 (48)	190
	HC≡CCON(CH ₃) ₂	(CH ₃) ₃ SnCu • DMS, THF, -78°	CH ₃ I, HMPA	 (87)	95
		(CH ₃) ₃ SnCu • DMS, THF, -78°	CH ₂ =CHCH ₂ Br, HMPA	 (82)	95
		(CH ₃) ₃ SnCu • DMS, THF, -78°	CH ₂ =C(CH ₃)CH ₂ Br, HMPA	 (81)	95
		(CH ₃) ₃ SnCu • DMS, THF, -78°	(<i>E</i>)-CH ₃ CH=C(CH ₃)CH ₂ Br, HMPA	 (78)	95
6	<i>trans</i> -CH ₃ CH=CHCON(CH ₃) ₂	<i>n</i> -C ₄ H ₉ Li, THF, -20° to rt	CH ₂ =CHCH ₂ Br	 (90)	190
		<i>n</i> -C ₄ H ₉ Li, THF, -20° to rt		 (86)	190

TABLE III. α,β -UNSATURATED AMIDES AND THIOAMIDES (Continued)

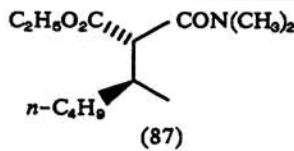
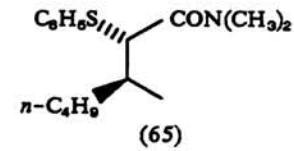
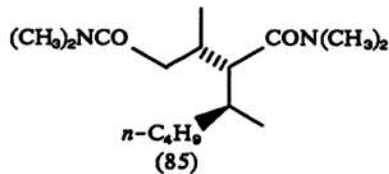
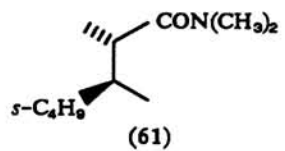
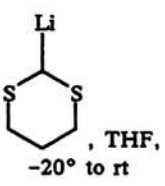
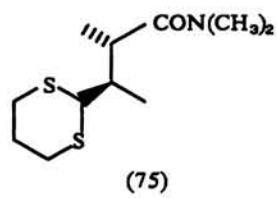
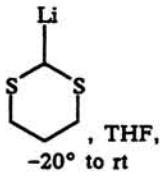
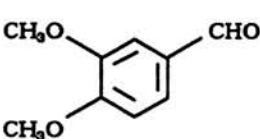
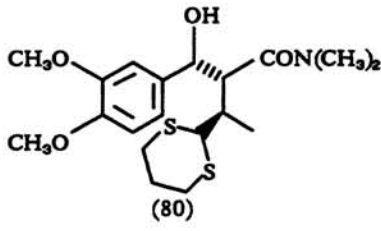
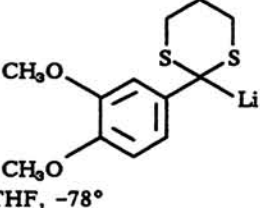
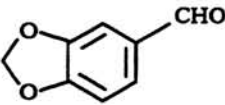
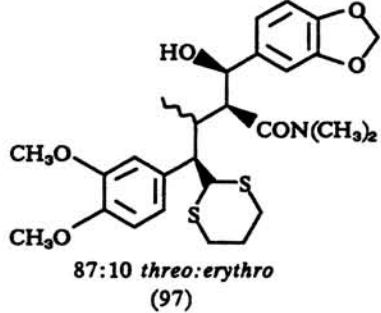
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Amides					
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, -20° to rt	$\text{C}_2\text{H}_5\text{O}_2\text{CCl}$	 (87)	190
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, -20° to rt	$(\text{C}_6\text{H}_5)_2\text{S}_2$	 (65)	190
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, -20° to rt	Self	 (85)	190
		$s\text{-C}_4\text{H}_9\text{Li}$, THF, -20° to rt	CH_3I	 (61)	190
		 , THF, -20° to rt	CH_3I	 (75)	190
		 , THF, -20° to rt		 (80)	190
		 , THF, -78°		 87:10 <i>threo:erythro</i> (97)	158

TABLE III. α,β -UNSATURATED AMIDES AND THIOAMIDES (Continued)

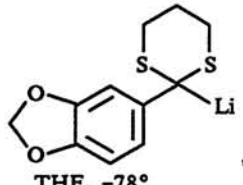
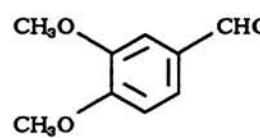
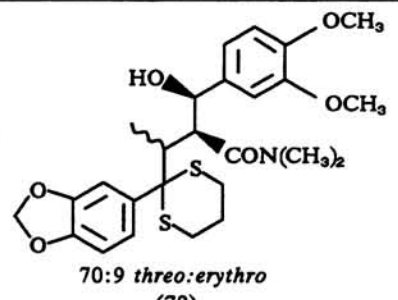
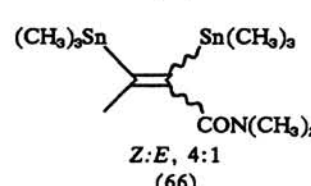
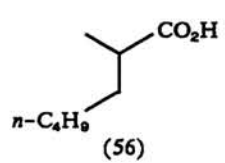
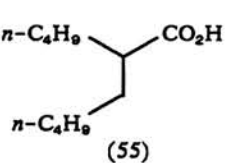
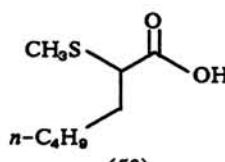
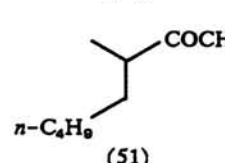
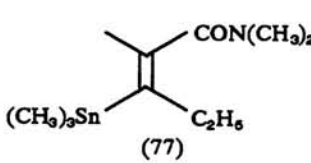
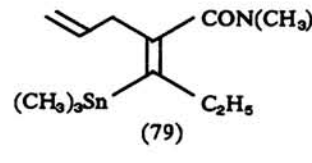
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Amides					
		THF, -78°		 70:9 <i>threo:erythro</i> (79)	158
	$\text{CH}_3\text{C}\equiv\text{CCON}(\text{CH}_3)_2$	$[(\text{CH}_3)_3\text{Sn}]_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF		 <i>Z:E</i> , 4:1 (66)	252
	$\text{CH}_2=\text{CHCON}(\text{CH}_3)\text{N}(\text{CH}_3)_2$	$n\text{-C}_4\text{H}_9\text{Li}$, THF, -78°	1) CH_3I 2) 10% HCl, reflux	 $n\text{-C}_4\text{H}_9$ (56)	193
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, -78°	1) $n\text{-C}_4\text{H}_9\text{Br}$ 2) 10% HCl, reflux	 $n\text{-C}_4\text{H}_9$ (55)	193
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, -78°	1) $(\text{CH}_3)_2\text{S}_2$ 2) 10% HCl, reflux	 $n\text{-C}_4\text{H}_9$ (53)	193
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, -78°	1) CH_3I 2) CH_3Li , HMPA, -78° to 0°	 $n\text{-C}_4\text{H}_9$ (51)	193
7	$\text{C}_2\text{H}_5\text{C}\equiv\text{CCON}(\text{CH}_3)_2$	$(\text{CH}_3)_3\text{SnCu} \cdot \text{DMS}$, THF, -78°	CH_3I , HMPA	 (77)	95
		$(\text{CH}_3)_3\text{SnCu} \cdot \text{DMS}$, THF, -78°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, HMPA	 (79)	95

TABLE III. α,β -UNSATURATED AMIDES AND THIOAMIDES (Continued)

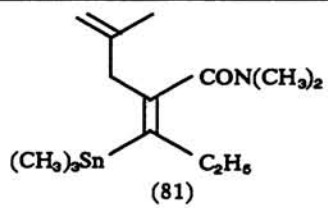
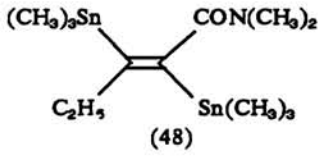
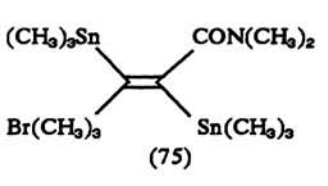
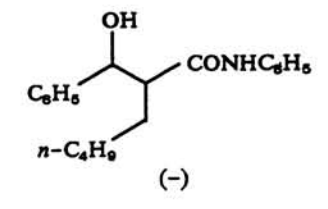
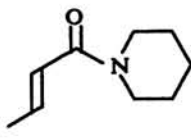
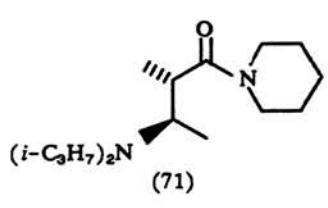
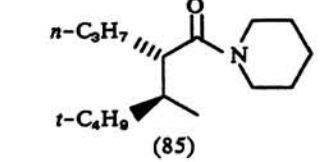
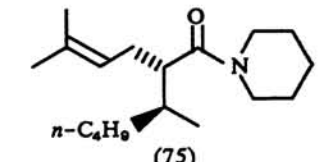
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Amides					
550		$(\text{CH}_3)_3\text{SnCu} \cdot \text{DMS}$, THF, -78°	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Br}$, HMPA	 (81)	95
		$[(\text{CH}_3)_3\text{Sn}]_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF	-	 (48)	252
8	$\text{Br}(\text{CH}_2)_3\text{C}\equiv\text{CCON}(\text{CH}_3)_2$	$[(\text{CH}_3)_3\text{Sn}]_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF	-	 (75)	252
9	$\text{CH}_2=\text{CHCONHC}_6\text{H}_5$	$n\text{-C}_4\text{H}_9\text{Li}$, THF/TMEDA, -65° to rt	$\text{C}_6\text{H}_5\text{CHO}$	 (-)	229
		LDA, THF, -70° to rt	CH_3I	 (71)	190
		$t\text{-C}_4\text{H}_9\text{Li}$, THF, -70° to rt	$n\text{-C}_3\text{H}_7\text{Br}$	 (85)	190
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, -70° to rt	$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{Br}$	 (75)	190

TABLE III. α,β -UNSATURATED AMIDES AND THIOAMIDES (Continued)

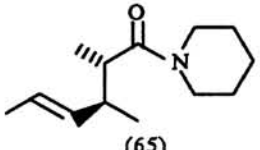
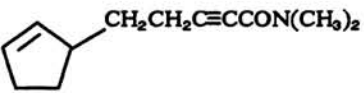
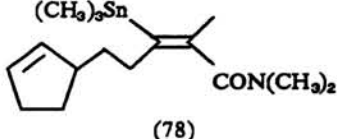
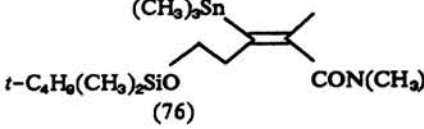
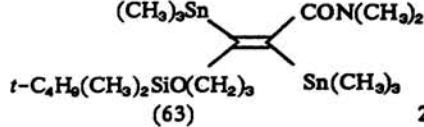
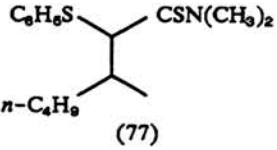
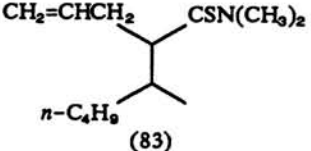
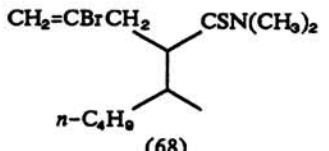
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Amides					
		$E\text{-CH}_3\text{CH=CHMgBr}$, THF, -20° to rt	CH_3I	 (65)	190
552 12		$(\text{CH}_3)_3\text{SnCu} \cdot \text{DMS}$, THF, -78°	CH_3I , HMPA	 (78)	95
13	$t\text{-C}_4\text{H}_9(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_2\text{C}\equiv\text{CCON}(\text{CH}_3)_2$	$(\text{CH}_3)_3\text{SnCu} \cdot \text{DMS}$, THF, -78°	CH_3I , HMPA	 (76)	95
14	$t\text{-C}_4\text{H}_9(\text{CH}_3)_2\text{SiO}(\text{CH}_2)_3\text{C}\equiv\text{CCON}(\text{CH}_3)_2$	$[(\text{CH}_3)_3\text{Sn}]_2$, $\text{Pd}[\text{C}_6\text{H}_5]_3)_4$, THF	-	 (63)	252
Section B: Thioamides					
	$(E)\text{-CH}_3\text{CH=CHCSN}(\text{CH}_3)_2$	$n\text{-C}_4\text{H}_9\text{Li}$, THF, 0°	$(\text{C}_6\text{H}_5)_2\text{S}_2$	 (77)	194
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, 0°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, 0°	 (83)	194
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, 0°	$\text{CH}_2=\text{CBrCH}_2\text{Br}$	 (68)	194

TABLE III. α,β -UNSATURATED AMIDES AND THIOAMIDES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Thioamides					
554	6 $\text{CH}_2=\text{C}(\text{CH}_3)\text{CSN}(\text{CH}_3)_2$	$n\text{-C}_4\text{H}_9\text{Li}$, THF, 0°	$\text{CH}_2=\text{CHCH}_2\text{Br}$	 (81)	194
		$\text{C}_2\text{H}_5\text{MgBr}$, THF, -78°	CH_3CHO	 (85)	191
		$\text{C}_2\text{H}_5\text{MgBr}$, THF, -78°	$i\text{-C}_3\text{H}_7\text{CHO}$	 (86)	191
		$\text{C}_2\text{H}_5\text{MgBr}$, THF, -78°	$\text{C}_6\text{H}_5\text{CHO}$	 +	191
				 41:59 (80)	
555		$\text{C}_2\text{H}_5\text{MgBr}$, THF, -78°	$\text{C}_6\text{H}_5\text{CHO}$	 +	191
				 8:92 (80)	
		$i\text{-C}_3\text{H}_7\text{MgBr}$, THF, -78°	CH_3CHO	 (95)	191

TABLE III. α,β -UNSATURATED AMIDES AND THIOAMIDES (Continued)

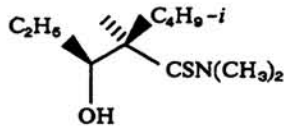
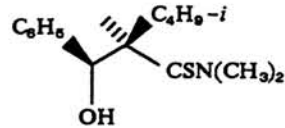
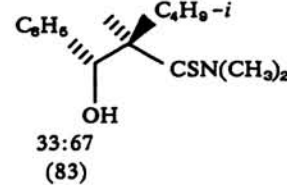
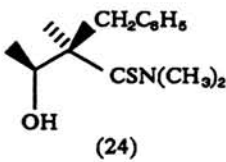
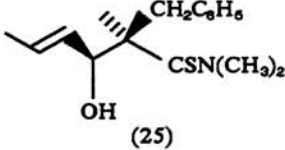
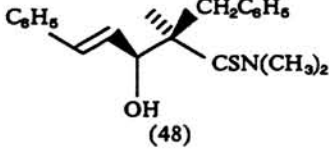
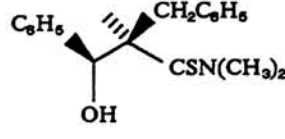
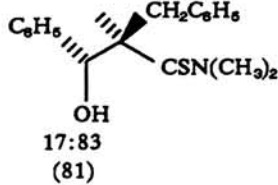
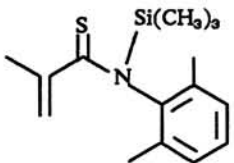
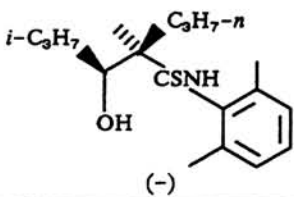
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Thioamides					
		$i\text{-C}_3\text{H}_7\text{MgBr}$, THF, -78°	$\text{C}_2\text{H}_5\text{CHO}$		191
556		$i\text{-C}_3\text{H}_7\text{MgBr}$, THF, -78°	$\text{C}_6\text{H}_5\text{CHO}$	 +	191
				 33:67 (83)	
		$\text{C}_6\text{H}_5\text{MgBr}$, THF, -78°	CH_3CHO	 (24)	191
		$\text{C}_6\text{H}_5\text{MgBr}$, THF, -78°	$(E)\text{-CH}_3\text{CH=CHCHO}$	 (25)	191
		$\text{C}_6\text{H}_5\text{MgBr}$, THF, -78°	$(E)\text{-C}_6\text{H}_5\text{CH=CHCHO}$	 (48)	191
557		$\text{C}_6\text{H}_5\text{MgBr}$, THF, -78°	$\text{C}_6\text{H}_5\text{CHO}$	 +	191
				 17:83 (81)	
15		$\text{C}_2\text{H}_5\text{MgBr}$, THF, -78°	$i\text{-C}_3\text{H}_7\text{CHO}$	 (-)	191

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES

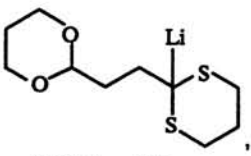
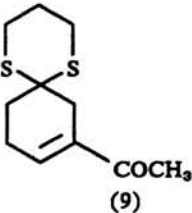
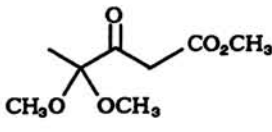
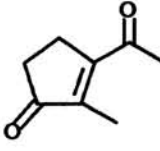
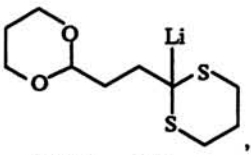
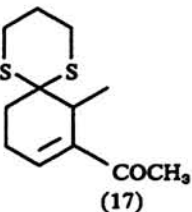
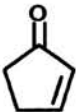
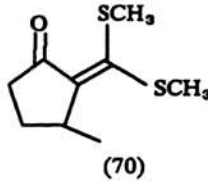
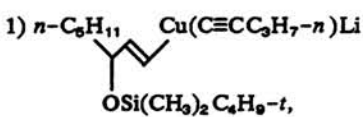
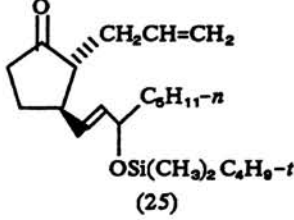
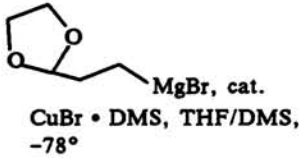
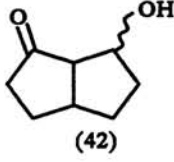
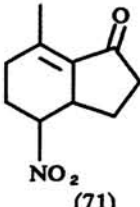
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
4	$\text{CH}_2=\text{CHCOCH}_3$	 HMPA, -78°	A	HCl/ CH_3OH , reflux	 (9)	404
		 $\text{CH}_3\text{OH}, (\text{C}_6\text{H}_5\text{CH}_2)(\text{CH}_3)_3\text{NOH}^{\pm}$	A	TsOH, toluene, reflux	 (30)	124
5	(<i>E</i>)- $\text{CH}_3\text{CH}=\text{CHCOCH}_3$	 HMPA, -78°	A	HCl/ CH_3OH , reflux	 (17)	404
		1) $(\text{CH}_3)_2\text{CuLi}$, -40° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) CH_3Li , THF/HMPA 2) CS_2 3) LHMDS, THF, CH_3I	 (70)	320
		1) $n\text{-C}_9\text{H}_{11}$  $\text{Cu}(\text{C}\equiv\text{CC}_9\text{H}_{17-n})\text{Li}$ OSi $(\text{CH}_3)_2\text{C}_4\text{H}_9-t$, -78° , HMPA 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$	S	1) LiNH_2 , THF, $\text{NH}_3(l)$ 2) $\text{CH}_2=\text{CHCH}_2\text{Br}$	 (25)	280
		 MgBr, cat. CuBr \cdot DMS, THF/DMS, -78°	A	HCl/ H_2O	 (42)	77
		$\text{CH}_3\text{CO}(\text{CH}_2)_3\text{NO}_2$, LDA, CHCl_3 , 60°	A	TsOH, C_6H_6 , reflux	 (71)	180

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		1) $(n-C_9H_{17})_2CuLi, -78^\circ$ 2) $(CH_3)_3SiCl, (C_2H_5)_3N$	S	$LiNH_2, THF/NH_3,$ $(Z)-CH_3O_2C(CH_2)_3CH=CHCH_2Br$	 (47)	339
		1) $(n-C_9H_{17})_2CuLi, -78^\circ$ 2) $(CH_3)_3SiCl, (C_2H_5)_3N$	S	$LiNH_2, THF/NH_3,$ $CH_3O_2C(CH_2)_3C\equiv CCH_2I$	 (19.5)	339
		1) $[(E)-n-C_9H_{17}CH=CH]_2CuLi, -40^\circ$ 2) $(CH_3)_3SiCl, (C_2H_5)_3N$	S	$LiNH_2, THF/NH_3,$ $(E)-CH_3O_2C(CH_2)_3CH=CHCH_2Br$	 (58)	339
		1) $(C_6H_5)_2CuLi, 0^\circ$ 2) $(CH_3)_3SiCl, (C_2H_5)_3N,$ rt	S	$CH_3Li, THF,$ $CH_2=CHCH_2Br$	 (42)	67
		1) $(C_6H_5)_2CuLi, 0^\circ$ 2) $(CH_3)_3SiCl, (C_2H_5)_3N,$ rt	S	$CH_3Li, THF,$ $C_6H_5Cu, 1 \text{ eq}$ $CH_2=CHCH_2Br$	" <i>trans:cis</i> , 4:96 (43)	67
		$NaOCH_3, CH_3OH$	A	$TsOH, \text{toluene},$ reflux	 (-)	124
		$THF, -78^\circ$	A	KH, rt, THF	 (55)	82

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

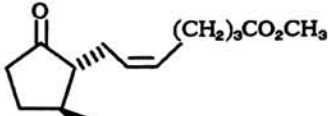
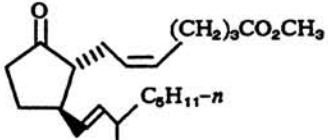
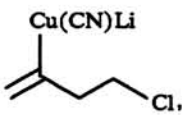
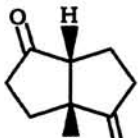
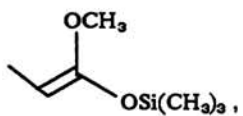
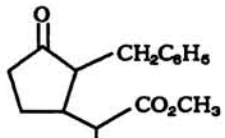
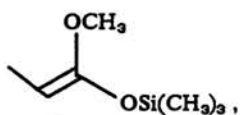
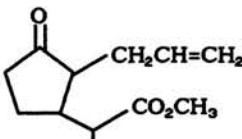
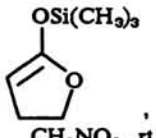
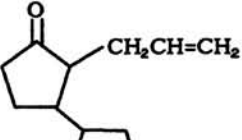
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
562		1) $\text{Li}_2\text{Cu}(\text{CH}=\text{CH}_2)_2\text{CN}$ 2) $\text{Si}(\text{CH}_3)_3\text{Cl}$	S	1) $n\text{-C}_4\text{H}_9\text{Li}$ 2) $\text{B}(\text{C}_2\text{H}_5)_3$ 3) $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{CH}_3$ $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$	 (57)	86
		1) $(n\text{-C}_6\text{H}_{11})_2\text{CuLi}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ 2) $\text{Si}(\text{CH}_3)_3\text{Cl}$	S	1) $n\text{-C}_4\text{H}_9\text{Li}$ 2) $\text{B}(\text{C}_2\text{H}_5)_3$ 3) $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{CH}_3$ $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$	 (54)	86
		$\text{Cu}(\text{CN})\text{Li}$ THF, -78°	A	KH, THF, rt	 4.9:1 <i>cis:trans</i> (52)	120
		TASF, THF, -70°	S	TASF, pyridine, THF, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	 (26)	131
563		TASF, THF, -70°	S	TASF, pyridine, THF, $\text{CH}_2=\text{CHCH}_2\text{Br}$	 (23)	131
		CH_3NO_2 , rt	S	TASF, pyridine, THF, $\text{CH}_2=\text{CHCH}_2\text{Br}$	 (13)	131

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		TBAF	S	TBAF, Br-CH ₂ -C≡C-CH ₂ -CH ₂ -O-THP		132
564		Cu(SC ₆ H ₅)Li, THF, -78°	A	450°, basic Al ₂ O ₃		405
		Cu(SC ₆ H ₅)Li, 0°	A	450°		406
		CH ₂ =CH-Cu(SC ₆ H ₅)Li	A	180°, intramolecular		121
6	(CH ₃) ₂ C=CHCOCH ₃	(CH ₃) ₃ Al, 3 mol % Ni(acac) ₂ , -50°		CH ₃ CHO, toluene		208
		(CH ₃) ₃ Al, 3 mol % Ni(acac) ₂ , -50°		C ₆ H ₅ CHO, toluene, -20°		208
565		(CH ₃) ₃ Al, 3 mol % Ni(acac) ₂ , -50°		(C ₆ H ₅) ₂ C=C=O, toluene		208
		1) (CH ₃) ₃ Al, 3 mol % Ni(acac) ₂ , -50° 2) toluene, 150°		1) CH ₃ CHO, C ₆ H ₆ 2) NH ₄ Cl/H ₂ O		208

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

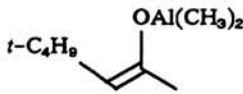
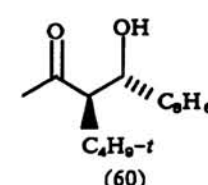
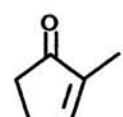
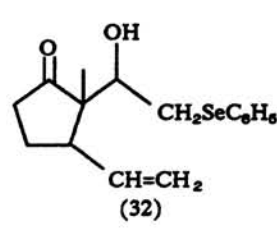
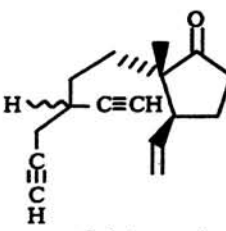
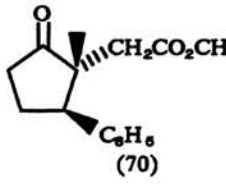
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
						
		1) $(\text{CH}_3)_3\text{Al}$, 3 mol % $\text{Ni}(\text{acac})_2$, -50° 2) toluene, 150°		1) $\text{C}_6\text{H}_5\text{CHO}$, C_6H_6 2) $\text{NH}_4\text{Cl}/\text{H}_2\text{O}$	 (60)	208
566		1) $(\text{CH}_2=\text{CH})_2\text{CuMgBr}$, THF, -70° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) CH_3Li , rt, 1.5 h 2) $\text{C}_6\text{H}_5\text{SeCH}_2\text{CHO}$, ZnCl_2 , 0° , 5 min	 (32)	377
		1) $\text{CH}_2=\text{CHMgBr}$, CuI , THF, -60° to -40°	S	1) LiNH_2 , $\text{NH}_3(\text{l})$, THF	 2:1 <i>trans:cis</i>	407 408
		2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA			(57)	290
		1) $(\text{CH}_2=\text{CH})_2\text{CuMgBr}$, THF, -70°	S	1) CH_3Li , THF/HMPA	" 4:1 <i>trans:cis</i> (37)	290
567		2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA		2) $\text{HC}\equiv\text{C}$		
		1) $(\text{C}_6\text{H}_5)_2\text{CuLi}$, 0° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$	S	CH_3Li , HMPA $\text{CH}_3\text{O}_2\text{CCH}_2\text{Br}$	 (70)	67

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

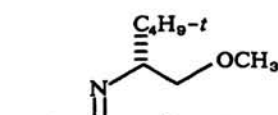
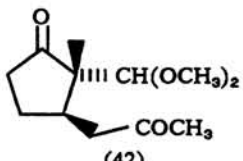
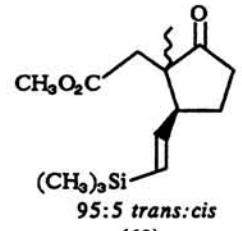
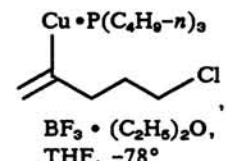
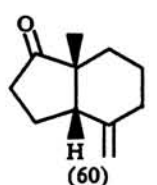
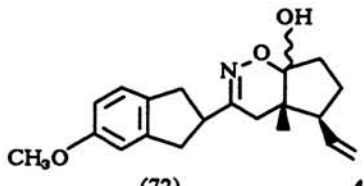
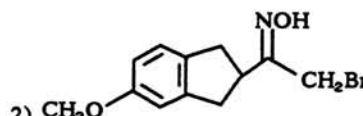
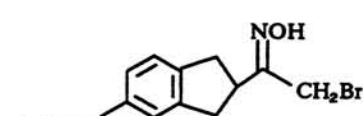
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		1) $(\text{C}_4\text{H}_9\text{-}t)_2\text{CuLi} \cdot \text{DMS}$, THF, -60° 2) $(\text{CH}_3)_3\text{SiCl}$	S	SnCl_4 , CH_2Cl_2 , $\text{HC}(\text{OCH}_3)_3$	 (42)	101
		1) $[(E)\text{-}(\text{CH}_3)_3\text{SiCH}=\text{CH}]_2\text{CuMgBr}$, THF, -70° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) CH_3Li 2) $\text{BrCH}_2\text{CO}_2\text{CH}_3$	 (68) 95:5 <i>trans:cis</i>	100
		 $\text{Cu} \cdot \text{P}(\text{C}_4\text{H}_9\text{-}n)_3$ $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, THF, -78°	A	KH, rt, THF	 (60)	82
		1) $n\text{-C}_3\text{H}_7\text{C}\equiv\text{CCu}(\text{CH}=\text{CH}_2)\text{Li}$, THF, HMPA, -60°	A	1) CH_3Li , THF	 (72)	409
				2) CH_3O -  - CH_2Br	"	
		1) $n\text{-C}_3\text{H}_7\text{C}\equiv\text{CCu}(\text{CH}=\text{CH}_2)\text{Li}$, THF, HMPA, -60°	S	1) CH_3Li , THF		409
		2) $(\text{CH}_3)_3\text{SiCl}$		2) CH_3O -  - CH_2Br	(74)	

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

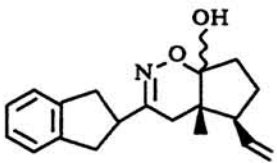
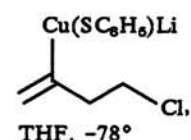
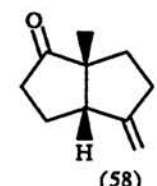
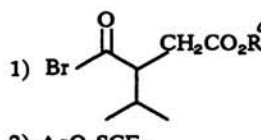
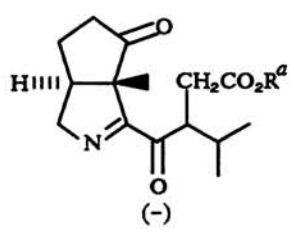
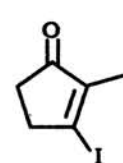
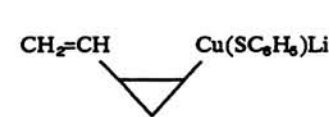
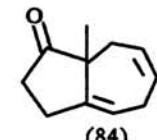
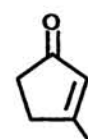
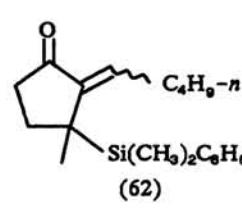
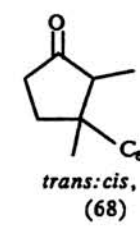
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		1) $n\text{-C}_3\text{H}_7\text{C}\equiv\text{CCu}(\text{CH}=\text{CH}_2)\text{Li}$, THF, HMPA, -60°	A	1) CH_3Li , THF	 (53)	409
		 THF, -78°	A	KH, THF, rt	 (58)	120
		1) LiCH_2NC 2) $(\text{CH}_3)_2\text{SiCl}$	S	1)  2) AgO_3SCF_3	 (-)	298
			A	180° , intramolecular	 (84)	121
		1) $[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{CuLi}$, THF, -23° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$	S	1) $n\text{-C}_4\text{H}_9\text{CHO}$, TiCl_4 , CH_2Cl_2 2) H^+ , C_6H_6 , reflux	 (62)	63
		$(\text{C}_6\text{H}_5)_2\text{CuLi}$, 0°	A	1) LDA, 1 eq, CuCN , CH_3I , HMPA	 <i>trans:cis</i> , 35:65 (68)	67
		1) $(\text{C}_6\text{H}_5)_2\text{CuLi}$, 0° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$	S	1) CH_3Li 2) CH_3I , HMPA	" <i>trans:cis</i> , 93:7 (22)	67

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

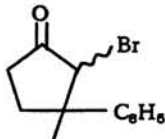
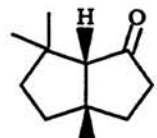
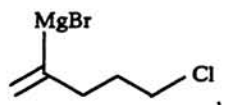
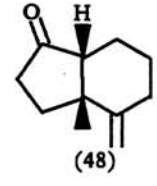
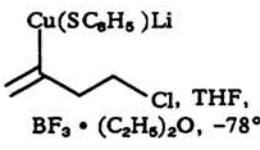
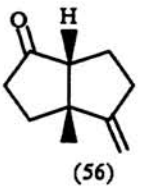
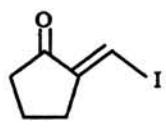
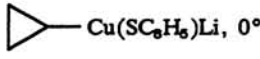
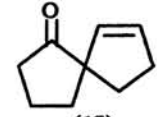
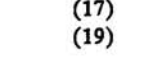
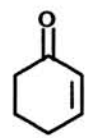
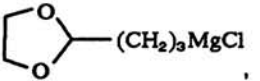
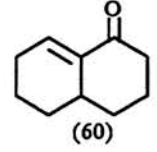
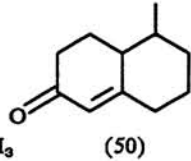
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
					”	
		1) $(C_6H_5)_2CuLi$, 0° 2) $(CH_3)_3SiCl$, $(C_2H_5)_3N$	S	CH_3Li , 2 mol % CH_3Cu , CH_3I , HMPA	<i>trans:cis</i> , 19:81 (35)	67
					”	
		1) $(C_6H_5)_2CuLi$ 2) Br_2 , -78°		$(CH_3)_2CuLi$, CH_3I , HMPA	<i>trans:cis</i> , 4:9 (64)	67
		1) $[CH_2=C(CH_3)CH_2CH_2]_2CuLi$, -40° 2) $(CH_3O_2C)_2O$	B	$SnCl_4$, CH_2Cl_2/H_2O	 (29)	410
		 25 mol % $CuBr \cdot DMS$, $BF_3 \cdot (C_2H_5)_2O$, THF, -78°	A	KH, THF, rt	 (48)	82
		 $Cu(SC_6H_5)_2Li$, THF, $BF_3 \cdot (C_2H_5)_2O$, -78°	A	KH, THF, rt	 (56)	120
		 $Cu(SC_6H_5)_2Li$, 0°	A	450°	 (17)  (19)	406 371
		 8 mol % $CuBr \cdot DMS$, THF/DMS, -78°	A	THF/ H_2O / HCl , reflux	 (60)	411
		1) $(CH_3)_2CuLi$, 0° 2) $(CH_3)_3SiCl$	S	1) CH_3Li 2) $CH_2=C[Si(CH_3)_3]COCH_3$ 3) CH_3OH/KOH	 (50)	277

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

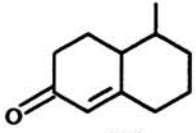
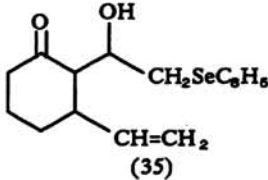
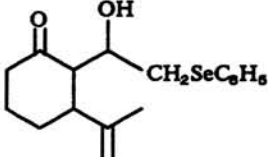
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		1) $(\text{CH}_3)_2\text{CuLi}$, 0° 2) $(\text{CH}_3)_3\text{SiCl}$	S	1) CH_3Li , 2) $\text{CuI} + \text{CH}_3\text{Li}$ 3) $\text{CH}_2=\text{C}[\text{Si}(\text{CH}_3)_3]\text{COCH}_3$ 4) $\text{CH}_3\text{OH}/\text{KOH}$	 (38)	277
					''	
		1) $(\text{CH}_3)_2\text{CuLi}$, 0° 2) $(\text{CH}_3)_3\text{SiCl}$	S	1) CH_3Li , CuI 2) $\text{CH}_2=\text{C}[\text{Si}(\text{CH}_3)_3]\text{COCH}_3$ 3) $\text{CH}_3\text{OH}/\text{KOH}$	(22)	277
					''	
		1) $(\text{CH}_3)_2\text{CuLi}$, 0° 2) $(\text{CH}_3)_3\text{SiCl}$	S	1) CH_3Li , then CH_3Cu 2) $\text{CH}_2=\text{C}[\text{Si}(\text{CH}_3)_3]\text{COCH}_3$ 3) $\text{CH}_3\text{OH}/\text{KOH}$	(49)	277
					''	
		1) $(\text{CH}_3)_2\text{CuLi}$, 0° 2) $(\text{CH}_3)_3\text{SiCl}$	S	1) CH_3Li , DME 2) $\text{CH}_2=\text{C}[\text{Si}(\text{CH}_3)_3]\text{COCH}_3$ 3) $\text{CH}_3\text{OH}/\text{KOH}$	(51)	277
					''	
		1) $(\text{CH}_3)_2\text{CuLi}$, 0° 2) $(\text{CH}_3)_3\text{SiCl}$	S	1) CH_3Li , THF 2) $\text{CH}_2=\text{C}[\text{Si}(\text{CH}_3)_3]\text{COCH}_3$ 3) $\text{CH}_3\text{OH}/\text{KOH}$	(46)	277
		1) $(\text{CH}_2=\text{CH})_2\text{CuMgBr}$, THF, -70° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) CH_3Li , 2) $\text{C}_6\text{H}_5\text{SeCH}_2\text{CHO}$, ZnCl_2	 (35)	377
		1) $[\text{CH}_2=\text{C}(\text{CH}_3)]_2\text{CuMgBr}$, THF, 0° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) CH_3Li , 2) $\text{C}_6\text{H}_5\text{SeCH}_2\text{CHO}$, 3) ZnCl_2	 (76)	377

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

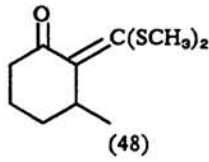
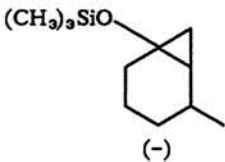
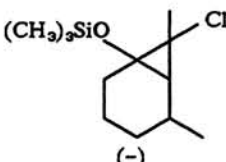
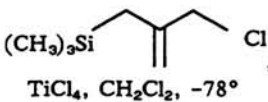
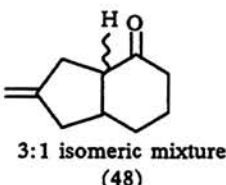
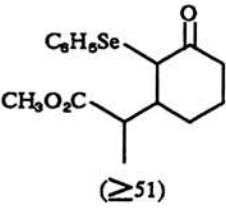
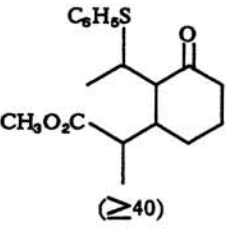
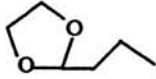
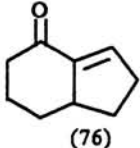
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
576		1) $(\text{CH}_3)_2\text{CuLi}$, -40° to 0° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) CH_3Li , THF/HMPA 2) CS_2 3) LHMDS, THF, CH_3I	 (48)	320
		1) $(\text{CH}_3)_2\text{CuLi}$ 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$	S	CH_2I_2 , $\text{Zn}(\text{Cu})$	 (-)	91
		1) $(\text{CH}_3)_2\text{CuLi}$ 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$	S	CH_3CHCl_2 , $n\text{-C}_4\text{H}_9\text{Li}$, -20°	 (-)	91
		TiCl_4 , CH_2Cl_2 , -78°	A	$\text{KOC}_4\text{H}_9\text{-}t$, $\text{HOC}_4\text{H}_9\text{-}t$	 3:1 isomeric mixture (48)	213
	$(E)\text{-CH}_3\text{CH}=\text{C}(\text{OCH}_3)\text{OSi}(\text{CH}_3)_3$, CH_3CN , 55°		S	$\text{C}_6\text{H}_5\text{SeCl}$, CH_2Cl_2	 (≥ 51)	412
577	$(E)\text{-CH}_3\text{CH}=\text{C}(\text{OCH}_3)\text{OSi}(\text{CH}_3)_3$, CH_3CN , 55°		S	$\text{C}_6\text{H}_5\text{SCH}(\text{Cl})\text{CH}_3$, ZnBr_2 , CH_2Cl_2	 (≥ 40)	412
		MgBr , cat. $\text{CuBr} \cdot \text{DMS}$, THF/DMS, -78° to 0°	A	$\text{HCl}/\text{H}_2\text{O}$	 (76)	77

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

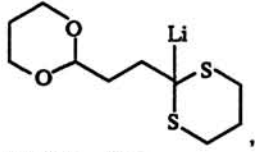
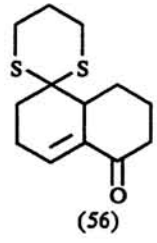
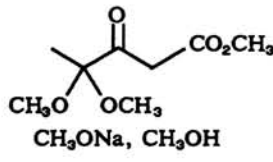
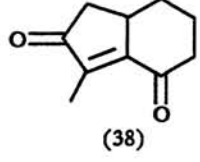
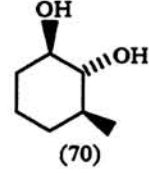
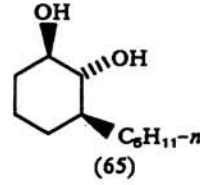
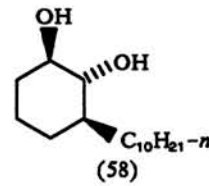
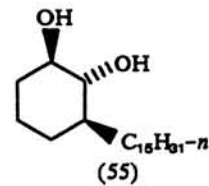
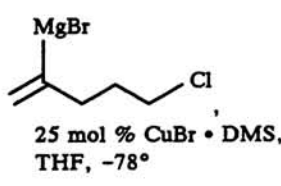
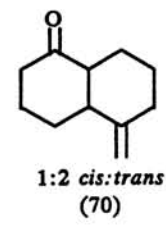
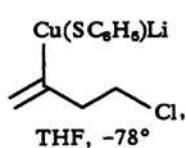
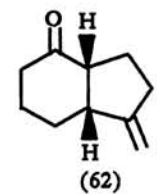
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		HMPA, -78°	A	HCl/CH ₃ OH, reflux	 (56)	404
		CH ₃ ONa, CH ₃ OH	A	TsOH, toluene, reflux	 (38)	124
		1) (CH ₃) ₂ CuLi, THF, -40° 2) (CH ₃) ₃ SiCl	S	1) BH ₃ , DMS 2) H ₂ O ₂ /-OH	 (70)	413
		1) (<i>n</i> -C ₈ H ₁₇) ₂ CuLi, THF, -40° 2) (CH ₃) ₃ SiCl	S	1) BH ₃ , DMS 2) H ₂ O ₂ /-OH	 (65)	413
		1) (<i>n</i> -C ₁₀ H ₂₁) ₂ CuLi, THF, -40° 2) (CH ₃) ₃ SiCl	S	1) BH ₃ , DMS 2) H ₂ O ₂ /-OH	 (58)	413
		1) (<i>n</i> -C ₁₆ H ₃₃) ₂ CuLi, THF, -40° 2) (CH ₃) ₃ SiCl	S	1) BH ₃ , DMS 2) H ₂ O ₂ /-OH	 (55)	413
		25 mol % CuBr • DMS, THF, -78°	A	KH, THF, rt,	 1:2 <i>cis:trans</i> (70)	82
		THF, -78°	A	KH, THF, rt,	 (62)	120

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
580		$\text{OSi(CH}_3)_3$, TASF, THF, -70°	S	TASF, pyridine, THF, $\text{CH}_2=\text{CHCH}_2\text{Br}$	 (18)	131
		, TASF, THF, -70°	S	TASF, pyridine, THF, $\text{CH}_2=\text{CHCH}_2\text{Br}$	 (≥ 17)	131
		$\text{Cu(SC}_6\text{H}_5)_2\text{Li}$, 0°	A	450°	 (-76)	406
		$\text{Cu(SC}_6\text{H}_5)_2\text{Li}$, $(\text{C}_2\text{H}_5)_2\text{O/THF}$, rt	A	Reflux, hexane	 (-90)	414
		$\text{Cu(SC}_6\text{H}_5)_2\text{Li}$, $(\text{C}_2\text{H}_5)_2\text{O/THF}$, rt	A	<i>o</i> - $\text{ClC}_6\text{H}_4\text{Cl}$, 220°	 (56)	414
581		$\text{Cu(SC}_6\text{H}_5)_2\text{Li}$, $(\text{C}_2\text{H}_5)_2\text{O/THF}$, -78° to rt	A	Reflux, xylene	 (≥ 90)	312
		$\text{Cu(SC}_6\text{H}_5)_2\text{Li}$, THF, -78°	A	1) 450° , basic Al_2O_3	 (72)	405
		$\text{Cu(SC}_6\text{H}_5)_2\text{Li}$	A	1) 425° , 2) Basic Al_2O_3	" (72)	371 121

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)


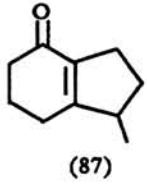
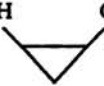
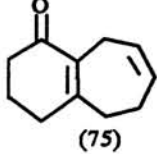

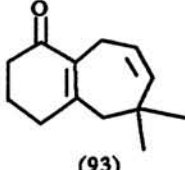

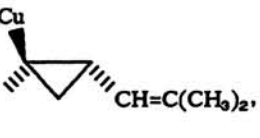
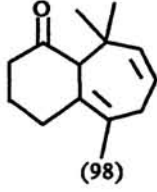
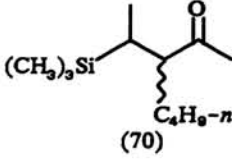
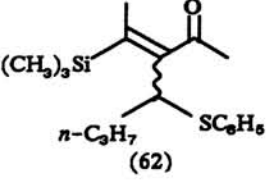
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		$\text{Cu}(\text{SC}_6\text{H}_5)\text{Li}$	A	1) 425° , 2) NaOCH_3	 (87)	371
	$\text{CH}_2=\text{CH}$ 	$\text{Cu}(\text{SC}_6\text{H}_5)\text{Li}$ -78°	A	180°	 (75)	121
	$\text{CH}_2=\text{CH}$ 	$\text{Cu}(\text{SC}_6\text{H}_5)\text{Li}$	A	110°	 (93)	121
	$\text{CH}_2=\text{CH}$ 	$\text{Cu}(\text{SC}_6\text{H}_5)\text{Li}$	A	222°	" (59)	121
	$\text{Li}(\text{C}_6\text{H}_5\text{S})\text{Cu}$ 	-78°	A	Xylene, reflux	 (98)	415
7	$(E)\text{-(CH}_3)_3\text{SiCH=CHCOCH}_3$	1) $(\text{CH}_3)_2\text{CuLi}$ 2) $(\text{CH}_3)_3\text{SiCl}$	S	1) $\text{C}_6\text{H}_5\text{SCHClC}_3\text{H}_7\text{-}n$, TiCl_4 2) Raney Ni	 (70)	251
	$(\text{CH}_3)_3\text{SiC}\equiv\text{CCOCH}_3$	1) $(\text{CH}_3)_2\text{CuLi}$ 2) $(\text{CH}_3)_3\text{SiCl}$	S	1) $\text{C}_6\text{H}_5\text{SCHClC}_3\text{H}_7\text{-}n$, ZnBr_2	 (62)	251

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

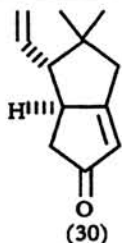
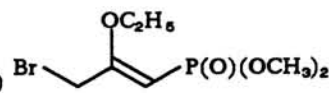
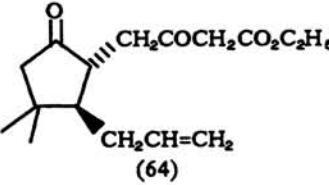
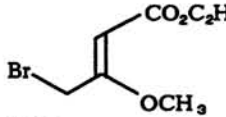
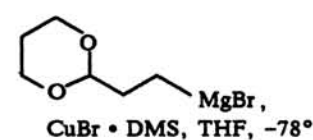
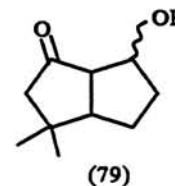
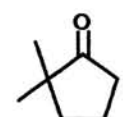
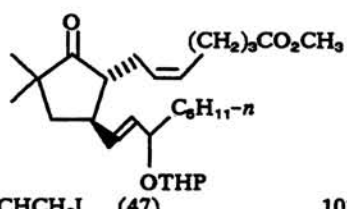
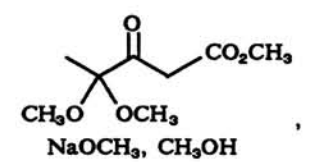
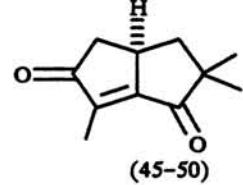
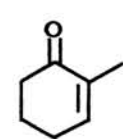
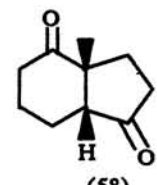
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		1) $\text{CH}_2=\text{CHMgBr}$, 10 mol % $\text{CuBr} \cdot \text{DMS}$, THF, -78°	S	1) CH_3Li , THF/ $(\text{C}_2\text{H}_5)_2\text{O}$	 (30)	281
		2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA		2)  $\text{P}(\text{O})(\text{OCH}_2\text{CH}_3)_2$, HMPA 3) H^+ , acetone 4) NaH , DME		
		1) $(\text{CH}_2=\text{CHCH}_2)_2\text{CuMgBr} \cdot \text{DMS}$, THF, -78°	S	1) LiNH_2 , THF/ NH_3 ,	 (64)	235
		2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$		2)  $\text{CO}_2\text{C}_2\text{H}_5$ OCH_3 3) HClO_4		
		MgBr , $\text{CuBr} \cdot \text{DMS}$, THF, -78°	A	HCl , aqueous acetone	 (79)	416
		$(n\text{-C}_8\text{H}_{17})_2\text{CuLi} \cdot \text{P}(\text{C}_4\text{H}_9\text{-}n)_3$, OTHP, -78°	A	LDA, THF, $(Z)\text{-CH}_3\text{O}_2\text{C}(\text{CH}_2)_3\text{CH}=\text{CHCH}_2\text{I}$	 (47)	103
		NaOCH_3 , CH_3OH	A	TsOH , toluene, reflux	 (45-50)	307 417
		$\text{Cu}(\text{CN})\text{Li}$, THF , -78°	A	KH , THF, rt	 (58)	120

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

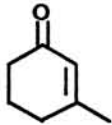
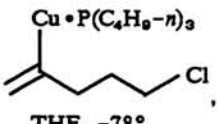
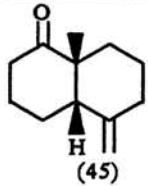
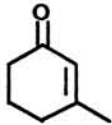
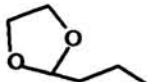
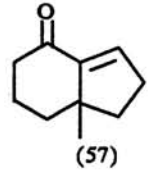
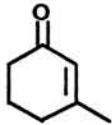
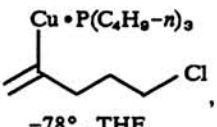
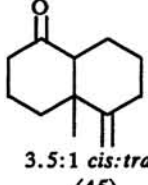
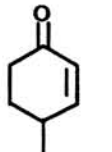
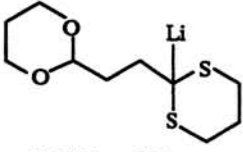
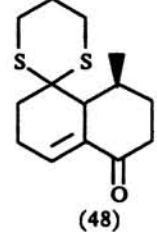
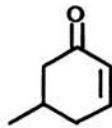
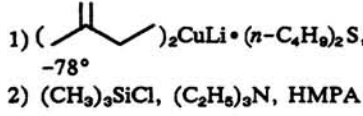
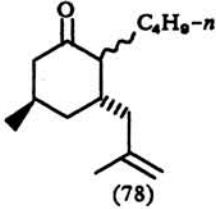
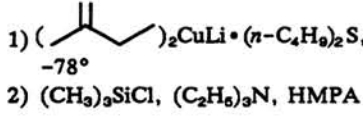
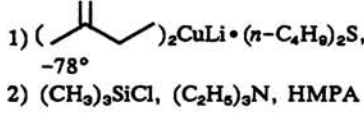
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
586		$\text{Cu} \cdot \text{P}(\text{C}_4\text{H}_9-n)_3$  THF, -78°	A	KH, THF, rt	 (45)	82
		 MgBr, cat. CuBr \cdot DMS, THF/DMS, -78° to 0°	A	HCl/H ₂ O	 (57)	77
		$\text{Cu} \cdot \text{P}(\text{C}_4\text{H}_9-n)_3$  -78° , THF	A	KH, THF, rt	 3.5:1 <i>cis:trans</i> (45)	82
		 Li HMPA, -78°	A	HCl/CH ₃ OH, reflux	 (48)	404
587		1)  -78° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) LiNH ₂ , THF 2) $n\text{-C}_4\text{H}_9\text{I}$	 (78)	64
					"	
		1)  -78° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) LiNH ₂ , 1.2 eq THF 2) $n\text{-C}_4\text{H}_9\text{I}$	(30)	64
					"	
		1)  -78° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) KNH ₂ , 1.2 eq THF 2) $n\text{-C}_4\text{H}_9\text{I}$	(42)	64

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

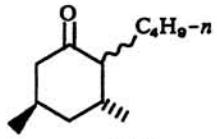
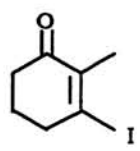
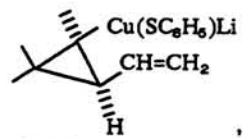
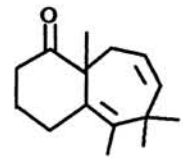
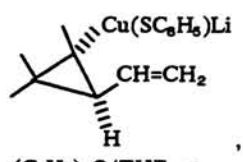
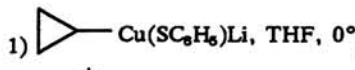
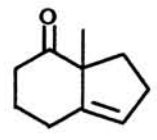
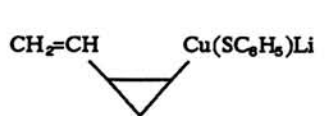
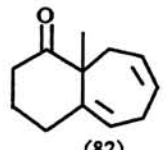
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
					"	
		1) $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CuLi} \cdot (n\text{-C}_4\text{H}_9)_2\text{S}$, -78° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) KNH_2 , THF 2) $n\text{-C}_4\text{H}_9\text{I}$	(48)	64
					"	
		1) $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CuLi} \cdot (n\text{-C}_4\text{H}_9)_2\text{S}$, -78° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) CH_3Li , THF 2) $n\text{-C}_4\text{H}_9\text{I}$, HMPA	(45)	64
					"	
		1) $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CuLi} \cdot (n\text{-C}_4\text{H}_9)_2\text{S}$, -78° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) CH_3Li , THF 2) $n\text{-C}_4\text{H}_9\text{I}$ HMPA	(36)	64
					"	
		1) $(\text{CH}_3)_2\text{CuLi}$, 0° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) LiNH_2 , THF 2) $n\text{-C}_4\text{H}_9\text{I}$	 (71)	64
		 $(\text{C}_2\text{H}_5)_2\text{O}/\text{THF}$, rt	A	Reflux, $o\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3$	 (46)	414
		 $(\text{C}_2\text{H}_5)_2\text{O}/\text{THF}$, rt	A	Reflux, $o\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3$	" (14)	414
		1)  2) H_3O^+	A	450°	 (-10)	405
			A	180°	 (82)	121

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
590		 $\text{Cu}(\text{SC}_6\text{H}_5)\text{Li}$	A	145° , collidine	 (37)	121
		 $\text{Cu}(\text{SC}_6\text{H}_5)\text{Li}$	A	222°	" (14)	121
		 $\text{Cu}(\text{SC}_6\text{H}_5)\text{Li}, 0^\circ$	A	450° or 1) LDA 2) $(\text{CH}_3)_3\text{SiCl}$ 3) 425°	 (26) (36) (40)	406 371 121
		 MgBr, cat. CuBr \cdot DMS, THF/DMS, -78° to 0°	A	HCl/H ₂ O	 (70)	77
		 NaOCH ₃ , CH ₃ OH	A	TsOH, toluene, reflux	 (59)	124
591		 LiCu $(\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9-t)_2$	A	1) NaH, THF 2)	 (51)	418
8		 MgBr, CuBr \cdot DMS, THF, -78°	A	HCl, aqueous acetone	 (48)	416

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
592		1) CuI • DMS, 0° 2) CH ₃ O ₂ CCl	B	1) CH ₃ Li, THF 2) (CH ₃) ₂ N ⁺ =CH ₂ Cl ⁻	 N(CH ₃) ₂ (51)	144
		1) CH ₂ =CH(CH ₂) ₃ MgBr, (C ₂ H ₅) ₂ O/DMS, 10 mol % CuI 2) CH ₃ O ₂ CCl, 0° to rt	B	1) <i>m</i> -CPBA, CH ₂ Cl ₂ 2) CH ₃ Li, THF 3) (CH ₃) ₂ N ⁺ =CH ₂ Cl ⁻ , CH ₃ I, K ₂ CO ₃	 (-)	419
		1) CH ₂ =CH(CH ₂) ₂ MgBr, 10 mol % CuI, (C ₂ H ₅) ₂ O/DMS, 0° to rt 2) (CH ₃) ₃ SiCl	S	1) CH ₃ Li, THF 2) (CH ₃) ₂ N ⁺ =CH ₂ Cl ⁻ , CH ₃ I, K ₂ CO ₃	 (42)	420
593		 THPO HMPA	A	1) NaH, C ₆ H ₆ , HCO ₂ C ₂ H ₅ 2) LDA, THF, CH ₃ I	 (45)	301
		 Cu(SC ₆ H ₅)Li, 0°	A	450°	 (23)	406
		 MgBr, 10 mol % CuI, THF, -20°	A	5% HCl, C ₂ H ₅ OH, reflux	 22:78 <i>cis:trans</i> (36)	91

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		 MgBr, then $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$	S	1) CH_3Li , DME 2) CH_3I	 (21)	91
		$\text{Cu}(\text{CN})\text{Li}$ Cl, THF, $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, -78°	A	KH, THF, rt	 (47)	120
9		$(n\text{-C}_6\text{H}_{11})_2\text{CuLi} \cdot \text{P}(\text{C}_4\text{H}_9\text{-}n)_3$ OTHP -78°	A	LDA, THF, -78° , $(Z)\text{-CH}_3\text{O}_2\text{C}(\text{CH}_2)_3\text{CH}=\text{CHCH}_2\text{I}$	 (6)	103
		$(\text{CH}_2)_4\text{CuLi}$, -45°	A	1) <i>m</i> -CPBA 2) <i>t</i> - $\text{C}_4\text{H}_9\text{OK}$, <i>t</i> - $\text{C}_4\text{H}_9\text{OH}$	 +	315
		MgBr Cl, 25 mol % $\text{CuBr} \cdot \text{DMS}$, $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, -78° , THF	A	KH, THF, rt	 8:1 <i>cis:trans</i> (40)	82
		$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CuMgBr} \cdot \text{BF}_3$, -78°	A	1) O_3 , $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ 2) $\text{HCl}/\text{H}_2\text{O}/\text{HOAc}$	 (44)	91

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		1) $(\text{CH}_2=\text{CH})_2\text{CuLi}$, DMS, -75° 2) $(\text{CH}_3)_3\text{SiCl}$, HMPA, $(\text{C}_2\text{H}_5)_3\text{N}$	S	1) O_3 , CH_3OH 2) aq. HCl		329
		1) $(\text{CH}_3)_2\text{CuLi}$, DMS, -75° 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$, HMPA	S	1) O_3 , CH_3OH 2) aq. HCl		329
10	$(\text{CH}_3)_3\text{SiC}\equiv\text{CCOC}_4\text{H}_9-t$	1) $(\text{CH}_3)_2\text{CuLi}$ 2) $(\text{CH}_3)_3\text{SiCl}$	S	$\text{C}_6\text{H}_5\text{S}-\text{CH}(\text{Cl})-\text{C}_3\text{H}_7-n$, TiCl_4		251
		$(n-\text{C}_6\text{H}_{11}-\text{CH}(\text{OTHP})-\text{CH}=\text{CH})_2\text{CuLi}\cdot\text{P}(\text{C}_6\text{H}_{11-n})_3$, -78°	A	1) LDA, THF 2) $(Z)-\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_3\text{CH}=\text{CHCH}_2\text{I}$ (6)		103
		$\text{MgBr}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl}$, 0.3 eq $\text{CuBr}\cdot\text{DMS}$, THF, -78°	A	KH, THF, rt		323
11		$\text{C}_2\text{H}_5\text{O}_2\text{CCHLiCH}_3$, $\text{CuI}\cdot\text{P}(\text{OCH}_3)_3$	A	1) NaH, THF 2) CH_3I		90
		$\text{C}_2\text{H}_5\text{O}_2\text{CCHLiCH}_3$, $\text{CuI}\cdot\text{P}(\text{OCH}_3)_3$	A	1) LDA, THF 2) CH_3I		90

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

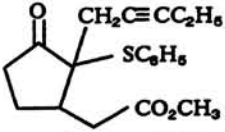
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
					"	
		$C_2H_5O_2CCHLiCH_3$, $CuI \cdot P(OCH_3)_3$	A	1) LDA, 1 eq HMPA, THF 2) CH_3I	(19)	90
					"	
		$C_2H_5O_2CCHLiCH_3$, $CuI \cdot P(OCH_3)_3$	A	1) LDA, 3 eq HMPA, THF 2) CH_3I	(35)	90
					"	
		$C_2H_5O_2CCHLiCH_3$, $CuI \cdot P(OCH_3)_3$	A	1) LICA, THF, 1 eq CuI 2) CH_3I , rt	(13)	90
					"	
		$C_2H_5O_2CCHLiCH_3$, $CuI \cdot P(OCH_3)_3$	A	1) LICA, 2 eq HMPA, THF 2) CH_3I	(25)	90
					"	
		$C_2H_5O_2CCHLiCH_3$, $CuI \cdot P(OCH_3)_3$	A	1) LTMP, 2 eq HMPA, THF 2) CH_3I	(39)	90
					"	
		$C_2H_5O_2CCHLiCH_3$, $CuI \cdot P(OCH_3)_3$	A	1) LHMDS, THF, 2) CH_3I	(22)	90
					"	
		$C_2H_5O_2CCHLiCH_3$, $CuI \cdot P(OCH_3)_3$	A	1) LHMDS, 2 eq HMPA, THF 2) CH_3I	(22)	90
					"	
		$CH_3O_2CCH_2CO_2CH_3$, $NaOCH_3$, CH_3OH , 0°	A	$C_2H_5C\equiv CCH_2Br$, NaH , DME	 <i>cis:trans</i> , 1.6:1 (53)	125

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

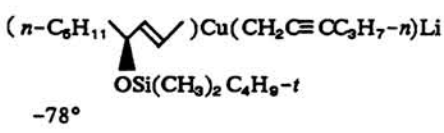
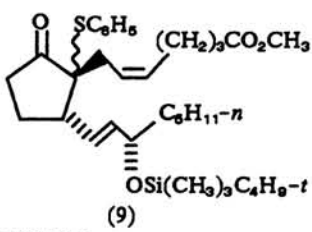
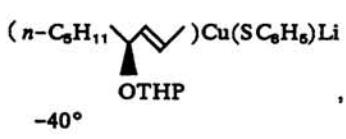
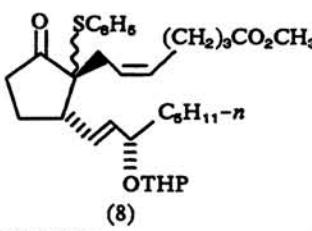
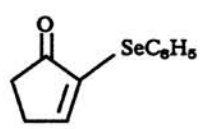
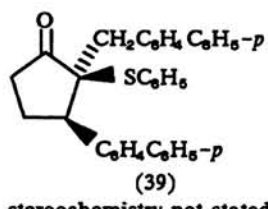
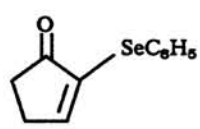
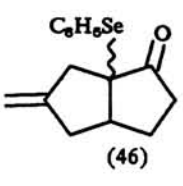
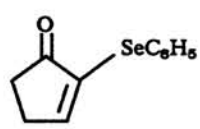
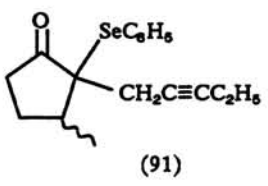
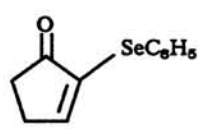
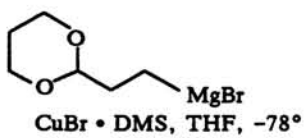
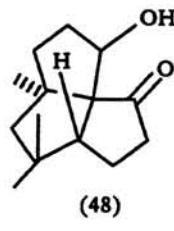
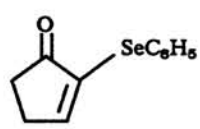
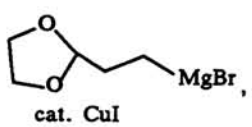
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
	 $(n\text{-C}_8\text{H}_{11})\text{Cu}(\text{CH}_2\text{C}\equiv\text{CC}_3\text{H}_7\text{-}n)\text{Li}$ $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ -78°	A	1) NaH, THF 2) (Z)- $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_9\text{CH}=\text{CHCH}_2\text{Br}$	 (9)	119	
	 $(n\text{-C}_8\text{H}_{11})\text{Cu}(\text{SC}_6\text{H}_5)\text{Li}$ OTHP -40°	A	1) NaH, THF 2) (Z)- $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_9\text{CH}=\text{CHCH}_2\text{Br}$	 (8)	119	
		$p\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{Li}$, cat. $[(n\text{-C}_4\text{H}_9)_3\text{P}]_4 \cdot \text{CuI}$, -78°	A	KH , DME, $p\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{CH}_2\text{Br}$	 (39) stereochemistry not stated explicitly	421
		$(\text{CH}_3)_3\text{Si}$ $\text{C}_2\text{H}_5\text{AlCl}_2$, CH_2Cl_2 , -78°	A	$\text{KOC}_4\text{H}_9\text{-}t$, 2/1 THF/ $t\text{-C}_4\text{H}_9\text{OH}$	 (46)	213
		$(\text{CH}_3)_2\text{CuLi}$, -20°	A	1) LDA, THF/HMPA 2) $\text{C}_2\text{H}_5\text{C}\equiv\text{CCH}_2\text{Br}$	 (91)	383
		 MgBr $\text{CuBr} \cdot \text{DMS}$, THF, -78°	A	HCl, H_2O /THF	 (48)	416
		 MgBr , cat. CuI	A	HCl/THF/ H_2O	"	326

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

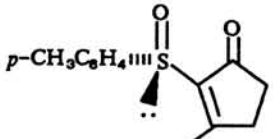
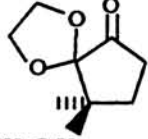
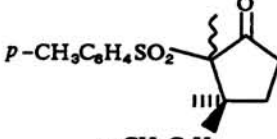
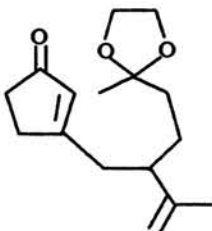
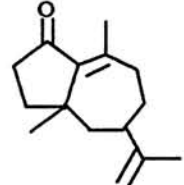
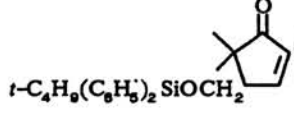
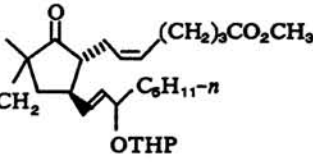
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
602		CuLi Cl , THF, $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$	A	KH, THF	 (69)	105
12		$\text{C}_6\text{H}_5\text{CH}_2\text{O}(\text{CH}_2)_4\text{MgBr}$, 8 mol % $\text{Cu}(\text{OAc})_2$, THF, -30°	A	1) $(\text{HOCH}_2)_2$, C_6H_6 , TsOH 2) LDA, THF, $\text{ClPO}[\text{N}(\text{CH}_3)_2]_2$ 3) Li, $\text{C}_2\text{H}_5\text{NH}_2$ 4) [O] 5) C_6H_6 , TsOH	 (64)	304
		$\text{CH}_2=\text{CHMgBr}$, ZnBr_2 , THF, -78°	A	1) NaH, DME, CH_3I 2) Al/Hg, THF/ H_2O	 <i>trans:cis</i> 92:8 (61)	386
		$\text{CH}_2=\text{CHMgBr}$, 1 mol % CuBr , THF, -78°	A	1) NaH, DME, CH_3I 2) Al/Hg, THF/ H_2O	 <i>trans:cis</i> 92:8 (61)	386
		1 eq ZnBr_2 , $\text{CH}_2=\text{CHMgBr}$, THF, -78° , 1 h	A	1) NaH, DME, CH_3I 2) $(\text{CH}_3)_2\text{CuLi}$, $t\text{-C}_4\text{H}_9\text{O}_2\text{CCH}_2\text{Br}$, HMPA	 $\text{CH}_2=\text{CH}$ (30)	192
		$(\text{CH}_3)_3\text{Si}$ Cl , TiCl_4 , CH_2Cl_2 , -78°	A	KOC_4H_9 , 2/1 THF/ $t\text{-C}_4\text{H}_9\text{OH}$ 0°	 (63)	213

602

12

603

TABLE IV. α,β -UNSATURATED KETONES VIA NEUTRAL INTERMEDIATES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
13		$(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{CuLi}$, THF, -78°	A	$(\text{HOCH}_2)_2$, TsOH, C_6H_6 , reflux	 $p\text{-CH}_3\text{C}_6\text{H}_4$ (50)	239
		$(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{CuLi}$, THF, -78°	A	1) <i>m</i> -CPBA 2) $\text{KOC}_4\text{H}_9\text{-}t$, CH_3I	 $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$ (25)	240
16		1) $(\text{CH}_3)_2\text{CuLi}$ 2) $(\text{CH}_3)_3\text{SiCl}$, $(\text{C}_2\text{H}_5)_3\text{N}$	S	TiCl_4 , CH_2Cl_2	 (54)	73
23		$(n\text{-C}_6\text{H}_{11})_2\text{CuLi}\cdot\text{P}(\text{C}_4\text{H}_9\text{-}n)_3$, OTHP, -78°	A	LDA, THF, $(Z)\text{-CH}_3\text{O}_2\text{C}(\text{CH}_2)_3\text{CH}=\text{CHCH}_2\text{I}$	 (39)	103

^a R = Undefined.

TABLE V. α,β -UNSATURATED ESTERS VIA NEUTRAL INTERMEDIATES

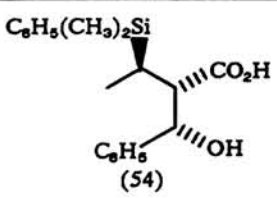
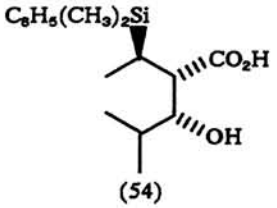
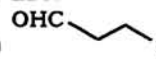
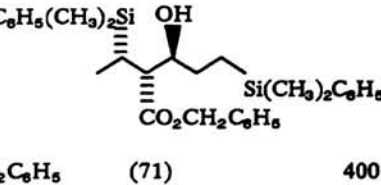
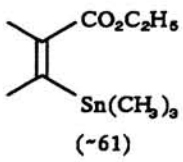

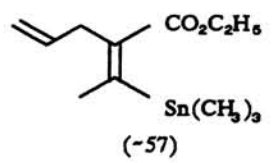
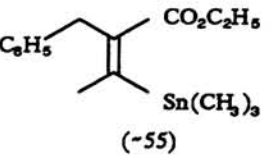
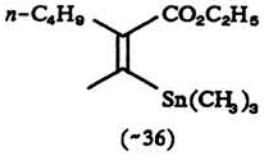
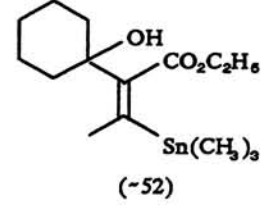
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s)	Ref.
4	<i>trans</i> -CH ₃ CH=CHCO ₂ CH ₂ CH=CH ₂	[C ₆ H ₅ (CH ₃) ₂ Si] ₂ CuLi	A	1) LDA 2) C ₆ H ₅ CHO 3) H ₂ /Pd		400
	<i>trans</i> -CH ₃ CH=CHCO ₂ CH ₂ C ₆ H ₅	[C ₆ H ₅ (CH ₃) ₂ Si] ₂ CuLi	A	1) LDA 2) <i>i</i> -C ₃ H ₇ CHO 3) H ₂ /Pd		400
		[C ₆ H ₅ (CH ₃) ₂ Si] ₂ CuLi	A	1) LDA 2) 		400
	CH ₃ C≡CCO ₂ C ₂ H ₅	(CH ₃) ₃ SnCu • DMS, THF, -48°	A	1) 1.1 eq CH ₃ Li, THF 2) CH ₃ I		94
		(CH ₃) ₃ SnCu • DMS, THF, -48°	A	1) 1.1 eq CH ₃ Li, THF 2) 		94
		(CH ₃) ₃ SnCu • DMS, THF, -48°	A	1) 1.1 eq CH ₃ Li 2) C ₆ H ₅ CH ₂ Br		94
		(CH ₃) ₃ SnCu • DMS, THF, -48°	A	1) 1.1 eq CH ₃ Li, THF 2) <i>n</i> -C ₄ H ₉ I		94
		(CH ₃) ₃ SnCu • DMS, THF, -48°	A	1) 1.1 eq CH ₃ Li, THF 2) cyclohexanone		94

TABLE V. α,β -UNSATURATED ESTERS VIA NEUTRAL INTERMEDIATES (Continued)

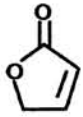
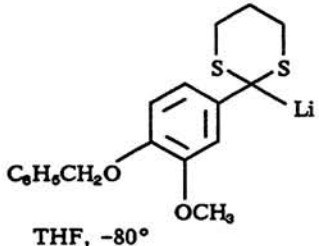
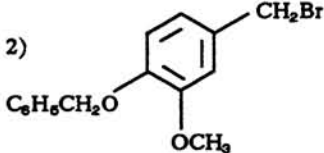
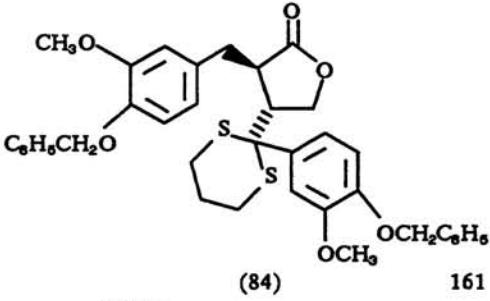
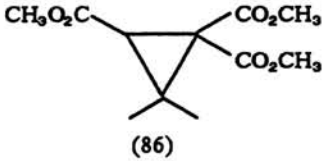
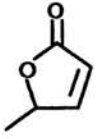
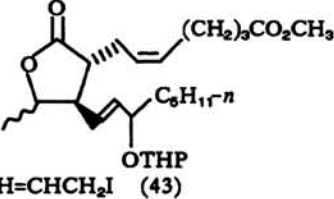
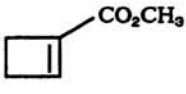
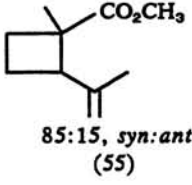
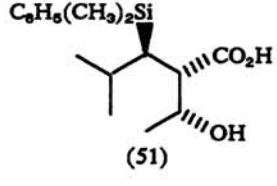
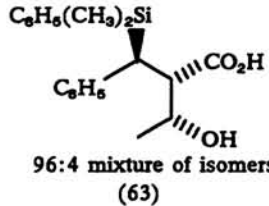
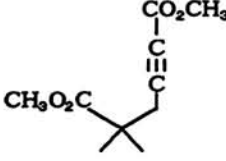
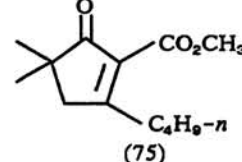
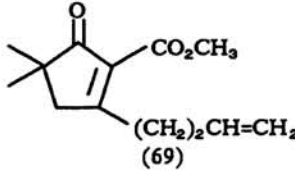
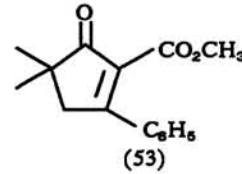
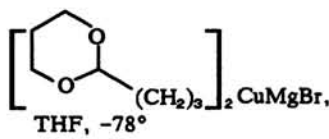
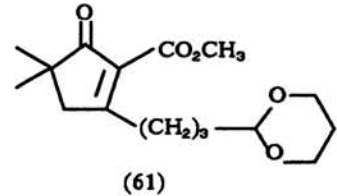
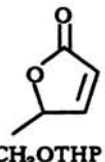
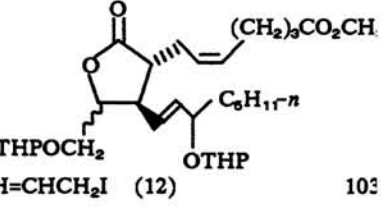
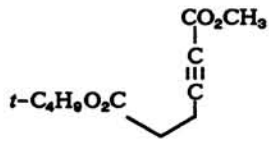
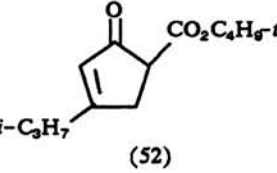
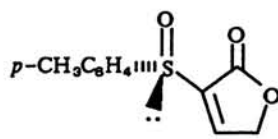
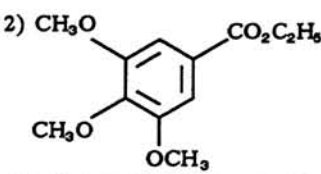
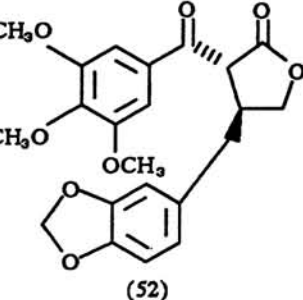
Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s)	Ref.
809		 THF, -80°	A	1) LDA 2) 	 (84)	161
5	$\text{CH}_3\text{O}_2\text{CCH}=\text{C}(\text{CO}_2\text{CH}_3)_2$	$\text{O}_2\text{NC}(\text{CH}_3)_2\text{Li}$, THF, 20°	A	NaH, DMSO	 (86)	178
		$(n\text{-C}_6\text{H}_{11})_2\text{CuLi}\cdot\text{P}(\text{C}_4\text{H}_9\text{-}n)_3$ OTHP -78°	A	LDA, THF, $(Z)\text{-CH}_3\text{O}_2\text{C}(\text{CH}_2)_3\text{CH}=\text{CHCH}_2\text{I}$ (43)	 (43)	103
		$\text{CH}_2=\text{C}(\text{CH}_3)\text{MgBr}$, 10 mol % CuI, THF, -70°	A	LDA, CH_3I , THF	 85:15, <i>syn:anti</i> (55)	75
609	6 $(E)\text{-}i\text{-C}_8\text{H}_7\text{CH}=\text{CHCO}_2\text{CH}_2\text{C}_6\text{H}_5$	$[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{CuLi}$	A	1) LDA 2) CH_3CHO 3) Pd/ H_2	 (51)	400
9	9 <i>trans</i> - $\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{CH}_2\text{C}_6\text{H}_5$	$[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]_2\text{CuLi}$	A	1) LDA 2) CH_3CHO 3) H_2/Pd	 96:4 mixture of isomers (63)	400

TABLE V. α,β -UNSATURATED ESTERS VIA NEUTRAL INTERMEDIATES (Continued)

Carbon No.	α, β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s)	Ref.
610		$(n-C_4H_9)_2CuLi$, THF, -78°	A	LDA, THF		99
		$(CH_2=CHCH_2CH_2)_2CuMgBr$, THF, -78°	A	LDA, THF		99
		$(C_2H_5)_2CuMgBr$, THF, -78°	A	LDA, THF		99
		 THF, -78°	A	LDA, THF		99
10		$(n-C_8H_{17})_2CuLi \cdot P(C_4H_9-n)_3$, -78°	A	LDA, THF, $(Z)-CH_3O_2C(CH_2)_3CH=CHCH_2I$ (12)		103
611		$(i-C_3H_7)_2CuMgCl$, THF, -78°	A	LDA, THF		99
	11		1) $ZnBr_2$, 2,5-dimethyl THF 2) Raney Ni	S	1) LDA, THF, HMPA 2) 	

^aSee addendum to Table V for additional entries.

TABLE VI. MISCELLANEOUS SUBSTRATES

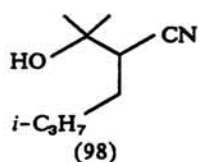
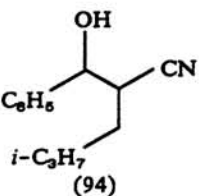
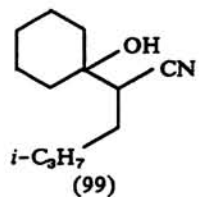
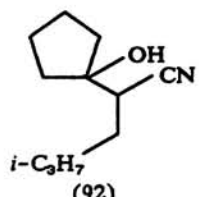
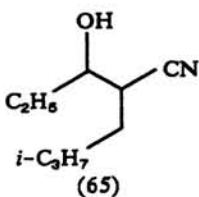
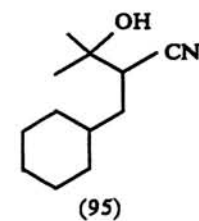
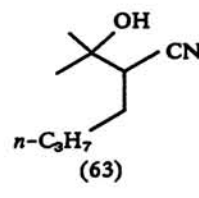
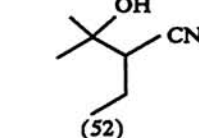
Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
3	$\text{CH}_2=\text{CHCN}$	$i\text{-C}_3\text{H}_7\text{I}$, Zn, CH_3CN , reflux	$(\text{CH}_3)_2\text{CO}$	 $i\text{-C}_3\text{H}_7$ (98)	257
			$\text{C}_6\text{H}_5\text{CHO}$	 $i\text{-C}_3\text{H}_7$ (94)	257
			Cyclohexanone	 $i\text{-C}_3\text{H}_7$ (99)	257
			Cyclopentanone	 $i\text{-C}_3\text{H}_7$ (92)	257
			$\text{C}_2\text{H}_5\text{CHO}$	 $i\text{-C}_3\text{H}_7$ (65)	257
		Cyclohexyl iodide, Zn, CH_3CN , reflux	$(\text{CH}_3)_2\text{CO}$	 (95)	257
		$n\text{-C}_3\text{H}_7\text{I}$, Zn, CH_3CN , reflux	$(\text{CH}_3)_2\text{CO}$	 $n\text{-C}_3\text{H}_7$ (63)	257
		CH_3I , Zn, CH_3CN , reflux	$(\text{CH}_3)_2\text{CO}$	 (52)	257

TABLE VI. MISCELLANEOUS SUBSTRATES (Continued)

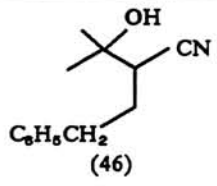

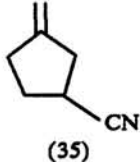
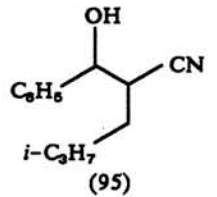
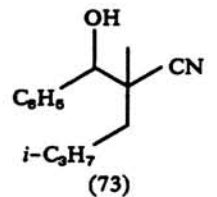
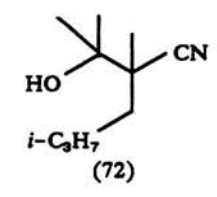
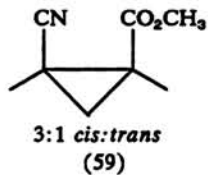
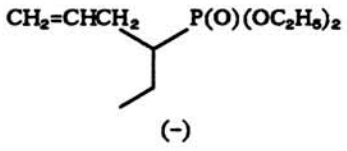
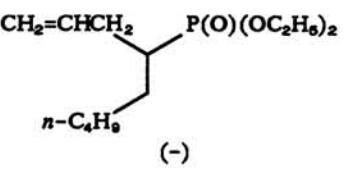
Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		$C_6H_5CH_2Br$, Zn, CH_3CN , reflux	$(CH_3)_2CO$	 (46)	257
614		$(CH_3)_3SiCH_2$  $CH_2O_2CCH_3$, $Pd[P(C_6H_5)_3]_4$ Toluene, 60°	Intramolecular	 (35)	215
4	(<i>E</i>)- $CH_3CH=CHCN$	<i>i</i> - C_3H_7I , Zn, CH_3CN , reflux	C_6H_5CHO	 (95)	257
	$CH_2=C(CH_3)CN$	<i>i</i> - C_3H_7I , Zn, CH_3CN , reflux	C_6H_5CHO	 (73)	257
		<i>i</i> - C_3H_7I , Zn, $(CH_3)_2CO$, reflux	$(CH_3)_2CO$	 (72)	257
		$CH_3O_2CCHClCH_3$, NaH, toluene	Intramolecular	 3:1 <i>cis:trans</i> (59)	279
615		$(CH_3)_2CuLi$	$CH_2=CHCH_2X$	 (-)	258
		$(n-C_4H_9)_2CuLi$	$CH_2=CHCH_2X$	 (-)	258

TABLE VI. MISCELLANEOUS SUBSTRATES (Continued)

Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		R_2CuLi	$R'X$	 (-) $R = CH_3, n-C_4H_9, n-C_6H_{17}$ $R' = CH_2=CHCH_2, CH_3, n-C_7H_{15}$	258
616		$(n-C_8H_{17})_2CuLi$ $OSi(CH_3)_2C_4H_9-t$	$CH_3O_2C(CH_2)_6I$	 (-)	258
		CH_3O_2C Triton B, C_8H_8	Intramolecular		146
7		CH_3O_2C Triton B, C_8H_8	Intramolecular		146
617		CH_3SO Li , THF, $-70^\circ, 1 h$	$(E)-C_8H_5CH=CHCHO$, reflux, 3 h	 (≥ 56)	165
		CH_3SO Li , THF, $-70^\circ, 1 h$	$(E)-n-C_8H_7CH=CHCHO$, reflux, 3 h	 (≥ 27)	165

TABLE VI. MISCELLANEOUS SUBSTRATES (Continued)

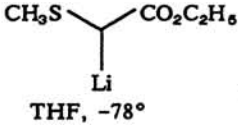
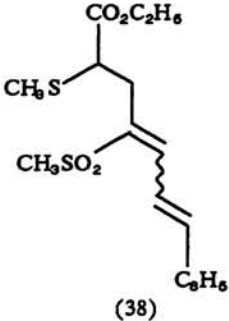
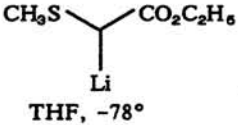
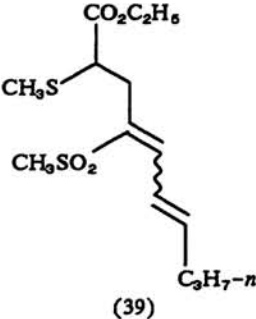
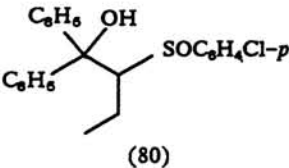
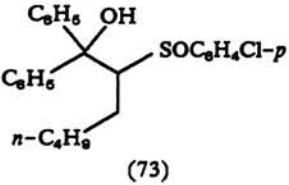
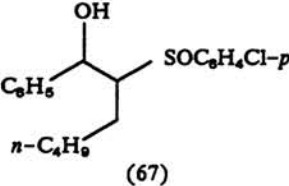
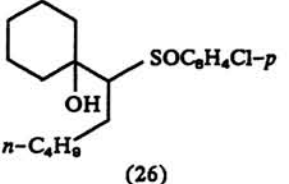
Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
618		 $\text{CH}_3\text{S}-\text{CH}(\text{Li})-\text{CO}_2\text{C}_2\text{H}_5$ THF, -78°	$(E)\text{-C}_6\text{H}_5\text{CH}=\text{CHCHO}$, rt, 30 min; then reflux, 3 h	 (38)	165
		 $\text{CH}_3\text{S}-\text{CH}(\text{Li})-\text{CO}_2\text{C}_2\text{H}_5$ THF, -78°	$n\text{-C}_3\text{H}_7\text{CH}=\text{CHCHO}$, rt, 30 min; then reflux, 3 h	 (39)	165
8	$\text{CH}_2=\text{CHSO}_2\text{C}_6\text{H}_4\text{Cl-}p$	$(\text{CH}_3)_2\text{CuLi}$, $(\text{C}_2\text{H}_5)_2\text{O/DMS}$, -60°	$(\text{C}_6\text{H}_5)_2\text{CO}$, -60° to rt	 (80)	98
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, $(\text{C}_2\text{H}_5)_2\text{O/DMS}$, -60°		 (73)	98
619		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, $(\text{C}_2\text{H}_5)_2\text{O/DMS}$, -60°	$\text{C}_6\text{H}_5\text{CHO}$, -60° to rt	 (67)	98
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, $(\text{C}_2\text{H}_5)_2\text{O/DMS}$, -60°	Cyclohexanone, -60° to rt	 (26)	98

TABLE VI. MISCELLANEOUS SUBSTRATES (Continued)

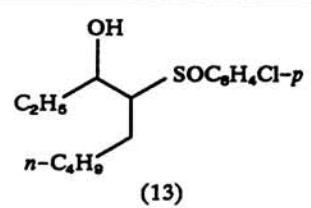
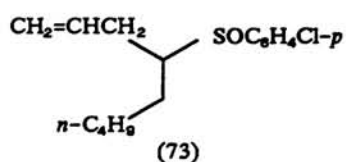
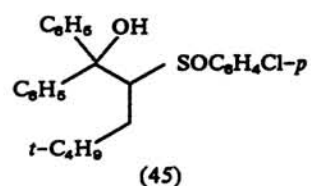
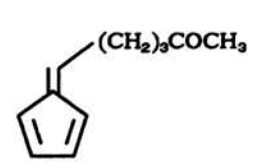
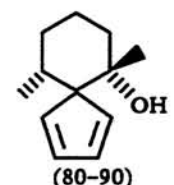
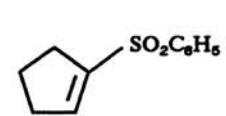
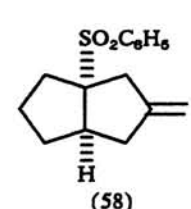
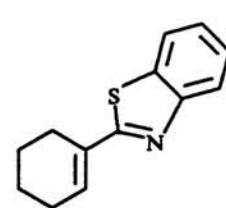
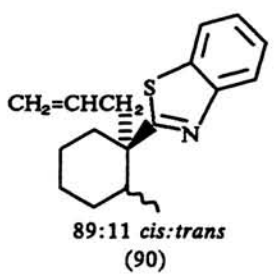
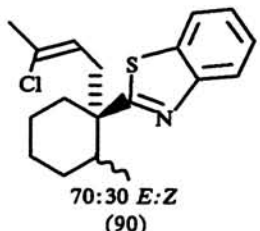
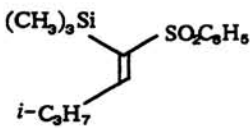
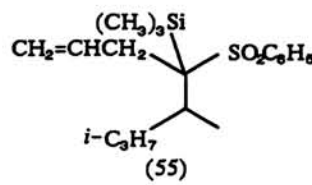
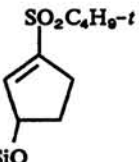
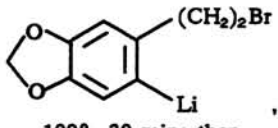
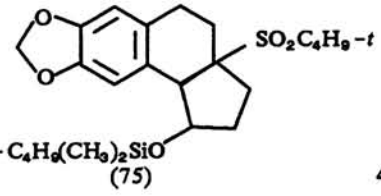
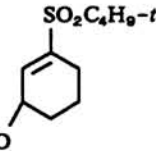
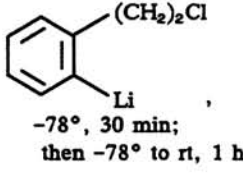
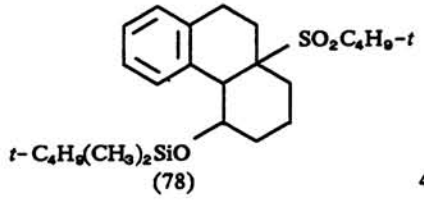
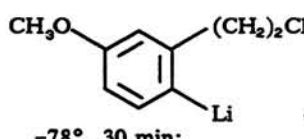
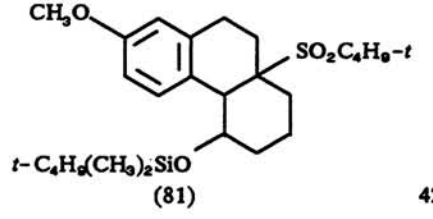
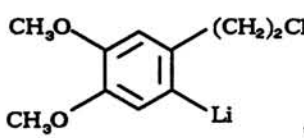
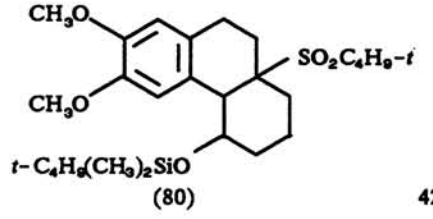
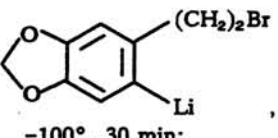

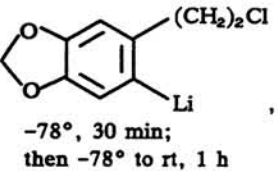
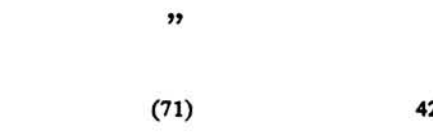
Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, $(\text{C}_2\text{H}_5)_2\text{O/DMS}$, -60°	$\text{C}_2\text{H}_5\text{CHO}$, -60° to rt	 (13)	98
		$(n\text{-C}_4\text{H}_9)_2\text{CuLi}$, $(\text{C}_2\text{H}_5)_2\text{O/DMS}$, -60°	$\text{CH}_2=\text{CHCH}_2\text{Br}$, -60° to rt	 (73)	98
		$(t\text{-C}_4\text{H}_9)_2\text{CuLi}$, $(\text{C}_2\text{H}_5)_2\text{O/DMS}$, -78°	$(\text{C}_6\text{H}_5)_2\text{CO}$, -60° to rt	 (45)	98
11		$(\text{CH}_3)_2\text{CuLi}$, -20°	Intramolecular	 (80-90)	244
		$(\text{CH}_3)_3\text{SiCH}_2$, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ THF, reflux	Intramolecular	 (58)	215
13		CH_3Li , HMPA, -78° , 160 min	$\text{CH}_2=\text{CHCH}_2\text{Br}$, -78° 20 min; then -78° to 25° , 30 min	 89:11 <i>cis:trans</i> (90)	261
		CH_3Li , HMPA, -78° , 160 min	$(Z)\text{-CH}_3\text{CCl}=\text{CHCH}_2\text{Cl}$, -78° , 80 min	 70:30 <i>E:Z</i> (90)	261

TABLE VI. MISCELLANEOUS SUBSTRATES (Continued)

Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
14		CH_3Li , THF, -78° , 10 min	$\text{CH}_2=\text{CHCH}_2\text{Br}$, -78° to rt	 (55)	423
15		 -100° , 30 min; then -100° to rt, 1 h	Intramolecular	 (75)	424
16		 -78° , 30 min; then -78° to rt, 1 h	Intramolecular	 (78)	424
		 -78° , 30 min; -78° to rt, 1 h	Intramolecular	 (81)	424
		 -100° , 30 min; then -100° to rt, 1 h	Intramolecular	 (80)	424
		 -100° , 30 min; then -100° to rt, 1 h	Intramolecular	 (79)	424
		 -78° , 30 min; then -78° to rt, 1 h	Intramolecular	 (71)	424

622

623

TABLE VI. MISCELLANEOUS SUBSTRATES (Continued)

Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
19		$\text{CH}_2=\text{C}(\text{CH}_3)\text{MgBr}$, THF	1) CH_3I , HMPA 2) citric acid 3) NaBH_4	 35:22 <i>trans:cis</i> (57)	262
624		$t\text{-C}_4\text{H}_9\text{Li}$, -78°	Intramolecular	 $\text{SO}_2\text{C}_4\text{H}_9\text{-}t$ (73)	425
		$\text{Li}-\text{CH}(\text{C}_6\text{H}_{11-n})-\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$, THF, -78°	$\text{I}-\text{CH}(\text{CO}_2\text{CH}_3)-\text{CH}=\text{CH}_2$, -40°	 $t\text{-C}_4\text{H}_9(\text{CH}_3)_2\text{SiO}$ (67)	282
					259
		$\text{Li}-\text{CH}(\text{C}_6\text{H}_{11-n})-\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$, THF, -78°	$\text{Br}-\text{CH}(\text{CO}_2\text{CH}_3)-\text{CH}=\text{CH}_2$	"	259
625		$\text{Li}-\text{CH}(\text{C}_6\text{H}_{11-n})-\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$, THF, -78°	$\text{Br}-\text{CH}=\text{CH}_2$	 $t\text{-C}_4\text{H}_9(\text{CH}_3)_2\text{SiO}$ (87)	259
		$\text{Li}-\text{CH}(\text{C}_6\text{H}_{11-n})-\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$, THF, -78°	$\text{Br}-\text{CH}(\text{CN})-\text{CH}=\text{CH}_2$	 $t\text{-C}_4\text{H}_9(\text{CH}_3)_2\text{SiO}$ (82)	259

TABLE VI. MISCELLANEOUS SUBSTRATES (Continued)

Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
626 20		$\text{C}_6\text{H}_5\text{COCHClLi}$, THF/DMF, -78° ; then 25° , 24 h	Intramolecular	$\text{C}_6\text{H}_5\text{CO}$ - (61)	263
		$\text{C}_6\text{H}_5\text{COCHBrLi}$, THF/DMF, -78° ; then 25° , 24 h	Intramolecular	" (70)	263
		$\text{C}_6\text{H}_5\text{COC}(\text{CH}_3)\text{ClLi}$, THF/DMF, -20° ; then 25° , 24 h	Intramolecular	" (53)	263
21		Li -	I -		259
627		Li -	I -		259
				$\text{Y} =$	(44)
				$\text{Y} =$	(72)

TABLE I. ALDEHYDES AND KETONES—ADDENDA

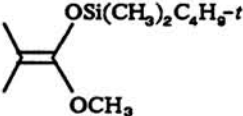
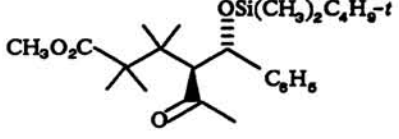
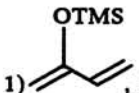
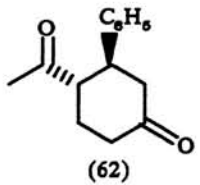
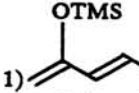
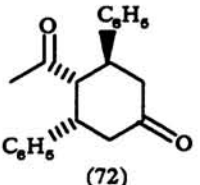
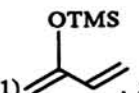
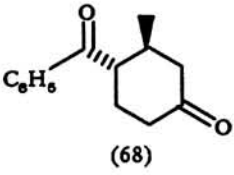
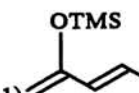
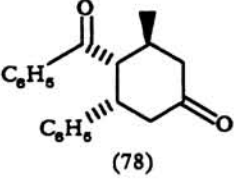
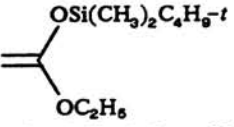
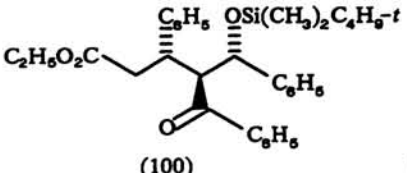
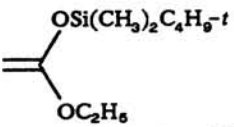
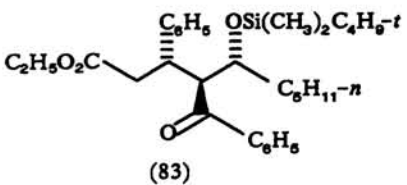
Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
6	$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$	 5 mol % trityl perchlorate, CH_2Cl_2 , -78°	$\text{C}_6\text{H}_5\text{CHO}$	 (74)	133
10	$(E)\text{-C}_6\text{H}_5\text{CH}=\text{CHCOCH}_3$	 1) C_6H_5 , 5-10 mol % trityl perchlorate, CH_2Cl_2 , -78° 2) H^+	Intramolecular	 (62)	134
		 1) C_6H_5 , 5-10 mol % trityl perchlorate, CH_2Cl_2 , -78° 2) H^+	Intramolecular	 (72)	134
	$(E)\text{-CH}_3\text{CH}=\text{CHCOC}_6\text{H}_5$	 1) C_6H_5 , 5-10 mol % trityl perchlorate, CH_2Cl_2 , -78° 2) H^+	Intramolecular	 (68)	134
		 1) C_6H_5 , 5-10 mol % trityl perchlorate, CH_2Cl_2 , -78° 2) H^+	Intramolecular	 (78)	134
15	$(E)\text{-C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5$	 5 mol % trityl perchlorate, CH_2Cl_2 , -78°	$\text{C}_6\text{H}_5\text{CHO}$	 (100)	133
		 5 mol % trityl perchlorate, CH_2Cl_2 , -78°	$n\text{-C}_6\text{H}_{11}\text{CHO}$	 (83)	133

TABLE I. ALDEHYDES AND KETONES—ADDENDA (Continued)

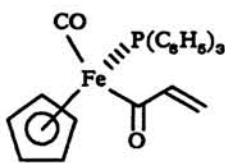
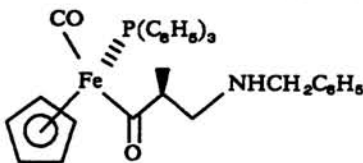
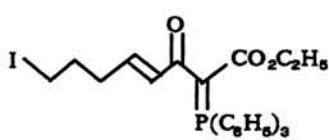
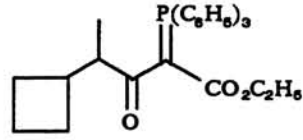
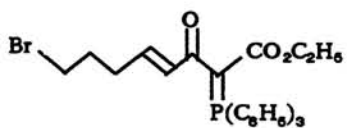
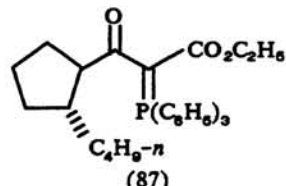
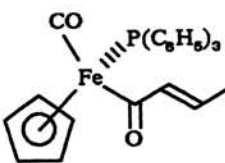
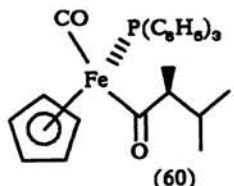
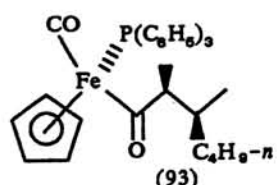
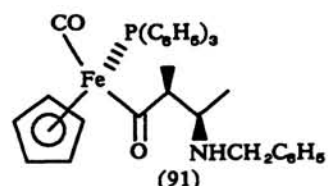
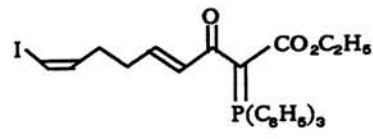
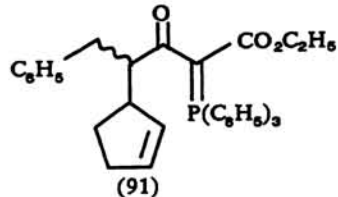
Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
27		$\text{C}_6\text{H}_5\text{CH}_2\text{NHLi}$, THF, -78°	CH_3I , -78°	 (13)	224
28		$t\text{-C}_4\text{H}_9\text{Li}$	CH_3I	 (73)	201
		$n\text{-C}_4\text{H}_9\text{Li}$	Intramolecular	 (87)	201
		CH_3Li , THF, -40°C , 2 h	CH_3I , 2 eq, -78° , 2 h	 (60)	225
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, -78° , 2 h	CH_3I , 2 eq, -78° , 2 h	 (93)	225
		$\text{C}_6\text{H}_5\text{CH}_2\text{NHLi}$, THF, -78° , 2 h	CH_3I , 4 eq, -78° , 1 h	 (91)	225
29		$t\text{-C}_4\text{H}_9\text{Li}$	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	 (91)	201

TABLE I. ALDEHYDES AND KETONES—ADDENDA (Continued)

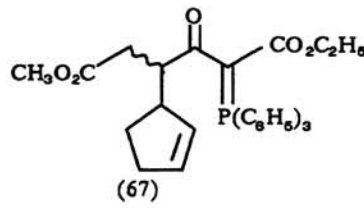
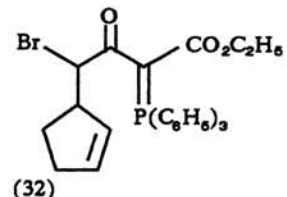
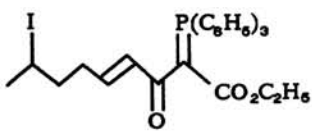
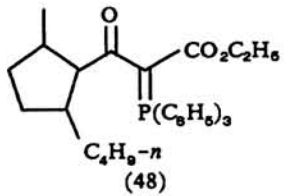
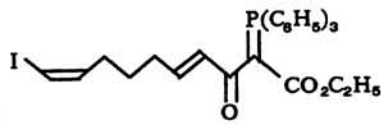
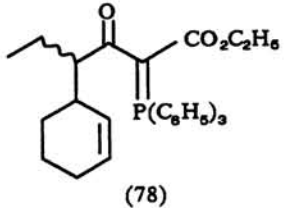
Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Acyclic Substrates					
632		$t\text{-C}_4\text{H}_9\text{Li}$	$\text{BrCH}_2\text{CO}_2\text{CH}_3$		201
		$n\text{-C}_4\text{H}_9\text{Li}$	Intramolecular		201
633		$t\text{-C}_4\text{H}_9\text{Li}$	$\text{C}_2\text{H}_5\text{I}$		201

TABLE I. ALDEHYDES AND KETONES—ADDENDA (Continued)


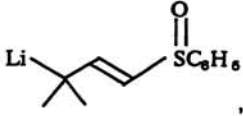
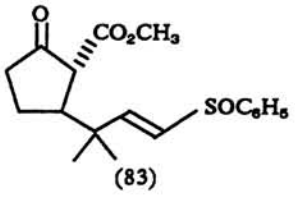
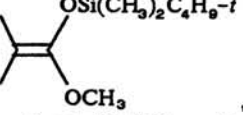
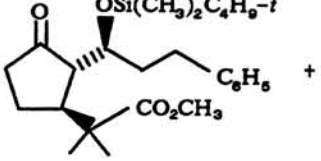
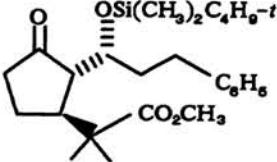

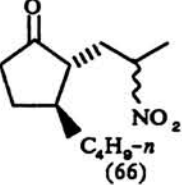
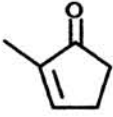
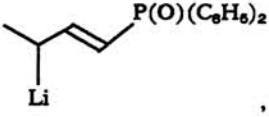
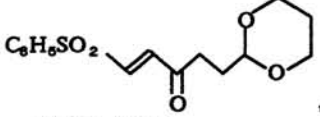
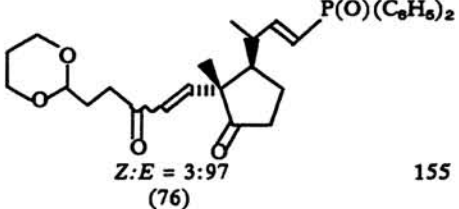
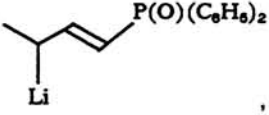
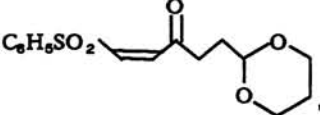
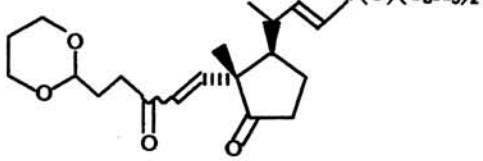
Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
5		 , THF	$\text{CH}_3\text{CO}_2\text{CN}$, -60°	 (83)	154
		5 mol % trityl perchlorate, CH_2Cl_2 , -78°	$\text{C}_6\text{H}_5(\text{CH}_2)_2\text{CHO}$	 +  88:12 (77)	133
		$n\text{-C}_4\text{H}_9\text{Cu} \cdot 2\text{P}(\text{C}_4\text{H}_9\text{-}n)_3$, -78°	 -78° , 20 min; -30° , 10 min; 0° 5 min	 $\text{C}_4\text{H}_9\text{-}n$ (66)	286
6		 , THF	 -20°C , 5 min	 $Z:E = 3:97$ (76)	155
		 , THF	 -20°C , 5 min	 $Z:E = 1:1$	155

TABLE I. ALDEHYDES AND KETONES—ADDENDA (Continued)

Carbon No.	α, β - Unsaturated Substrate	Nucleophilic Reagent and Cond.	Electrophilic Reagent and Cond.	Product(s) and Yield(s) (%)	Ref.	
Section B: Cyclic Substrates						
636		$\text{P(O)(C}_6\text{H}_5)_2$, THF			155	
		$\text{P(O)(C}_6\text{H}_5)_2$, THF			155	
		 5 mol % trityl perchlorate, CH_2Cl_2 , -78°	$\text{C}_6\text{H}_5(\text{CH}_2)_2\text{CHO}$	 91:9 (63)	133	
637		1) 2) H^+	Intramolecular perchlorate, CH_2Cl_2 , -78°C	 4:1 (74) + isomer	134	
7		1) 2) H^+	$\text{P(O)(C}_6\text{H}_5)_2$, 5-10 mol % trityl perchlorate, CH_2Cl_2 , -78°C	Intramolecular	 (55)	134

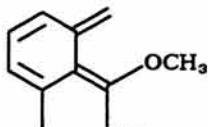
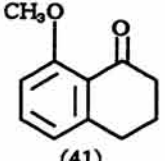
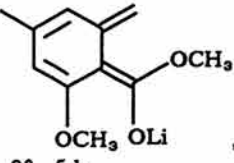
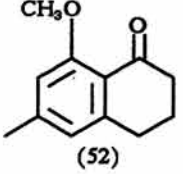
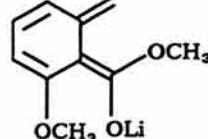
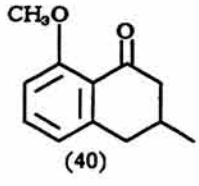
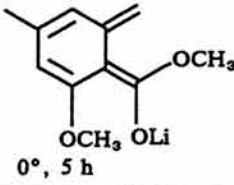
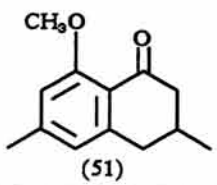
TABLE I. ALDEHYDES AND KETONES—ADDENDA (Continued)

Carbon No.	α , β - Unsaturated Substrate	Nucleophilic Reagent and Cond.	Electrophilic Reagent and Cond.	Product(s) and Yield(s) (%)	Ref.
Section B: Cyclic Substrates					
		 $n\text{-C}_8\text{H}_{17}$, $\text{Cu}\cdot 2\text{P}(\text{C}_4\text{H}_9\text{-}n)_3$, $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ -78° to -40°	$\text{CH}_2=\text{CHNO}_2$, -78° , 30 min; -40° , 30 min	 (27) $t\text{-C}_4\text{H}_9(\text{CH}_3)_2\text{SiO}$, $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$, $n\text{-C}_8\text{H}_{17}$ 286	
		 $n\text{-C}_8\text{H}_{17}$, $\text{Cu}\cdot 2\text{P}(\text{C}_4\text{H}_9\text{-}n)_3$, $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$	 NO_2 , CO_2CH_3	 (71) $t\text{-C}_4\text{H}_9(\text{CH}_3)_2\text{SiO}$, $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$, $n\text{-C}_8\text{H}_{17}$, CO_2CH_3 286	
		 $n\text{-C}_4\text{H}_9$, $\text{Cu}\cdot 2\text{P}(\text{C}_4\text{H}_9\text{-}n)_3$, $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$	 NO_2 , CO_2CH_3	 (57) $t\text{-C}_4\text{H}_9(\text{CH}_3)_2\text{SiO}$, $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$, $n\text{-C}_4\text{H}_9$, CO_2CH_3 286	
		 $n\text{-C}_4\text{H}_9$, $\text{Cu}\cdot 2\text{P}(\text{C}_4\text{H}_9\text{-}n)_3$, $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$	1) NO_2 2) 25% aq TiCl_3 , NH_4OAc	 (52) $t\text{-C}_4\text{H}_9(\text{CH}_3)_2\text{SiO}$, $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$, $n\text{-C}_4\text{H}_9$, CO_2CH_3 286	
		 $n\text{-C}_8\text{H}_{17}$, $\text{Cu}\cdot 2\text{P}(\text{C}_4\text{H}_9\text{-}n)_3$, $\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9\text{-}t$ -78°C	 NO_2 , CO_2CH_3 -78° , 15 min; -40° , 1 h	 (42) $t\text{-C}_4\text{H}_9(\text{CH}_3)_2\text{SiO}$, $\text{OSi}(\text{CH}_3)_2\text{-}t\text{-C}_4\text{H}_9$, $n\text{-C}_8\text{H}_{17}$ 285	

TABLE II. ESTERS AND LACTONES—ADDENDA

Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Electrophilic Reagent and Conditions	Product(s) and Yield(s) (%)	Ref.
Section A: Esters					
3		$(i\text{-C}_4\text{H}_9)_2\text{AlH}$, HMPA, THF, 0°, 1 h			211
6		NaOC_2H_5 , $\text{C}_2\text{H}_5\text{OH}$, 10–15°, 2 h	Cyclohexanone		297
7		NaOC_2H_5 , $\text{C}_2\text{H}_5\text{OH}$, 10–15°, 2 h	Cyclohexanone		297
		NaOC_2H_5 , $\text{C}_2\text{H}_5\text{OH}$, 10–15°, 2 h	Cyclohexanone		297
8		NaOC_2H_5 , $\text{C}_2\text{H}_5\text{OH}$, 10–15°, 2 h	Cyclohexanone		297
9		NaOC_2H_5 , $\text{C}_2\text{H}_5\text{OH}$, 10–15°C, 2h	Cyclohexanone		297

TABLE V. ESTERS—ADDENDA

Carbon No.	α , β -Unsaturated Substrate	Nucleophilic Reagent and Conditions	Neutral Intermediate Type	Electrophilic Reagent and Conditions	Product(s) and Yield(s)	Ref.
3	$\text{CH}_2=\text{CHCO}_2\text{CH}_3$	 1) OCH_3 OLi, THF, 0° , 5 h 2) NH_4Cl	A	HCl/ CH_3OH , reflux	 (41)	300
		 0° , 5 h	A	HCl/ CH_3OH , reflux	 (52)	300
4	$(E)\text{-CH}_3\text{CH}=\text{CHCO}_2\text{CH}_3$	 1) OCH_3 OLi, THF, 0° , 5 h 2) NH_4Cl	A	HCl/ CH_3OH , reflux	 (40)	300
		 0° , 5 h	A	HCl/ CH_3OH , reflux	 (51)	300

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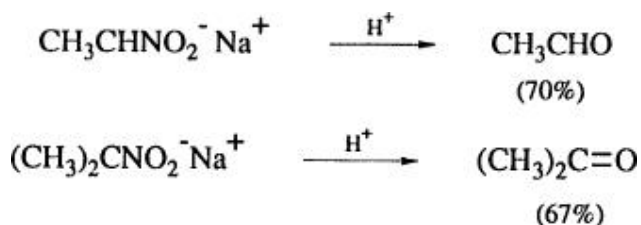
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The Nef Reaction

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1. Introduction

The Nef reaction is usually defined as the conversion of a primary or secondary nitroalkane into the corresponding carbonyl compound. (1) This reaction was reported by the Swiss chemist J. U. Nef in 1894 with two examples. (2)

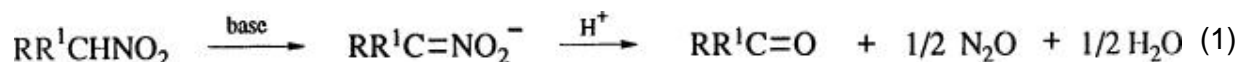


Hydrochloric and sulfuric acid give the same result. The conversion of a nitro group to a carbonyl group has become an important synthetic tool (3) because of the ease of preparation of substituted nitro compounds by condensation of nitroalkanes with aldehydes (the Henry reaction), (4) conjugate addition of nitroalkanes to electrophilic alkenes, 3c,5 or carbon alkylation of the dianion of primary nitroparaffins. (6) The Nef reaction is one of the better examples of “umpolung” reactivity in which the original nitro compound anion functions as an acyl anion equivalent. (7)

This chapter discusses the Nef reaction and modifications of the original process that extend the variety of compounds which are useful as substrates. Each modification is considered according to general mechanistic type and is organized in a “reagent” approach. The Tabular Survey lists all known examples of both the Nef reaction and these modifications so that specific comparison of methods can be made.

2. Mechanism

The mechanism of the Nef reaction has been studied extensively. (1, 8-18)
 The initial conversion of the nitro compound into the salt (“nitronate”) is accomplished with base; however, the key step is acidification of this intermediate to give the carbonyl compound and inorganic byproducts (Eq. 1).
 The latter



reaction is pH-dependent, and side reactions can occur (see Table A). (16)
 Weakly acidic conditions favor regeneration of the nitro compound, whereas high acidity gives the Nef reaction. (17) Oximes and pseudonitroles (α -nitroso nitro compounds) are observed at intermediate levels of acidity (pH 1–5).

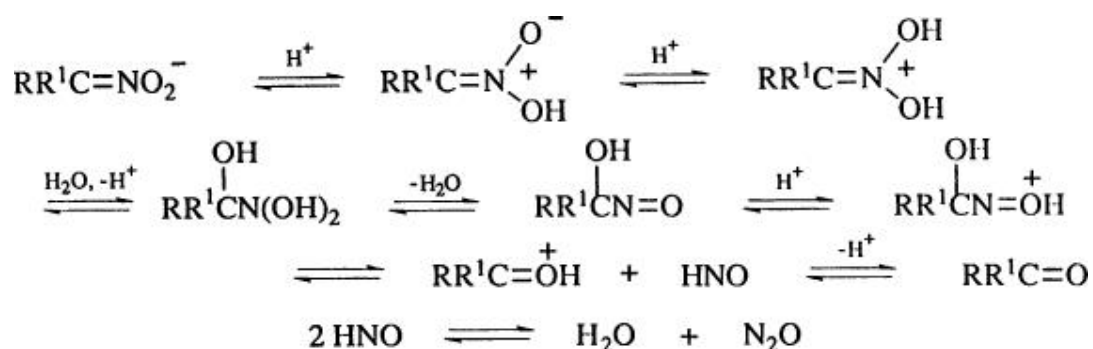
Table A. pH Dependence of the Product Distribution in the Acidification of the Salt of 2-Nitropropane at 21° (16)

pH	Yield (%)			
	(CH ₃) ₂ CHNO ₂	(CH ₃) ₂ C = O	(CH ₃) ₂ C = NOH	(CH ₃) ₂ C(NO)NO ₂
5.4	(100)	(0)	(0)	(0)
5.0	(85)	(8)	(8)	(0)
4.3	(44)	(20)	(19)	(15)
3.1	(10)	(30)	(30)	(29)
2.0	(0)	(39)	(32)	(29)
1.5	(0)	(49)	(28)	(22)
1.2	(0)	(80)	(12)	(7)
0.5	(0)	(100)	(0)	(0)

Several mechanisms have been proposed for this reaction. (8, 11, 15, 18)
 Kinetic analysis, together with the fact that additional water in an alcohol–water

solvent slows the reaction, (18) have led to the conclusion that two mechanisms can operate—the difference between the two mechanisms being the timing of water loss. The basic steps are sequential protonation of the nitronate salt on each oxygen followed by attack of water and decomposition of the resulting intermediate (Scheme 1). Another report contends that the nitronic acid is not an intermediate from the protonation of the nitronate. (19) Nevertheless, it is clear that the reaction is sensitive to both pH and concentration of water. As a result, adding acid to the nitronate favors nitro compound regeneration in competition with the Nef reaction, whereas addition of the nitronate to strong acid favors the Nef reaction. (20, 21) The mechanism clearly shows that additional side reactions can be expected in some systems because of nitrous oxide formation.

Scheme 1.



3. Scope and Limitations

3.1. Nitro Compounds and Nitronates

Nitro compounds are readily available (1, 22-29) and serve as ideal synthetic intermediates. The most common method of preparation is by nitrite ion displacement of a leaving group. (22) Most primary and secondary halides react with sodium nitrite in aprotic media such as dimethyl sulfoxide (DMSO) or



dimethylformamide (DMF) to give useful yields of the nitro compounds. In another approach, stabilized carbanions can be nitrated by treatment with a nitrate ester (RONO_2). (22, 24) In addition, enol acetates are nitrated by acetyl nitrate. (24, 25) Thus α -nitroketones, α -nitroesters, and β -nitrosulfones are easily prepared. A third method is the oxidation of primary amines with potassium permanganate, *m*-chloroperoxybenzoic acid (MCPBA), (22) ozone, (23) or the exotic dimethyldioxirane. (26) These oxidative methods are useful for preparing virtually any nitro compound—even tertiary derivatives that are not available by the nitrite displacement reaction, an $\text{S}_{\text{N}}2$ process. Oximes also can be oxidized with peroxyacids. (27, 28) Alternatively, oximes can be brominated to give α -bromo nitroso compounds, which can be oxidized with nitric acid/3. This is a valuable route for preparing secondary nitroparaffins by reductive removal of the bromine. (29, 30) These latter compounds also can be obtained in good yields by alkylation of the dianions of primary nitro compounds. (6) Another recent method uses hypochlorous acid to chlorinate oximes in 71–93% yields, and the products are then reduced with magnesium, zinc, or hydrogen/palladium to give 77–95% yields of secondary nitro compounds. (29a)

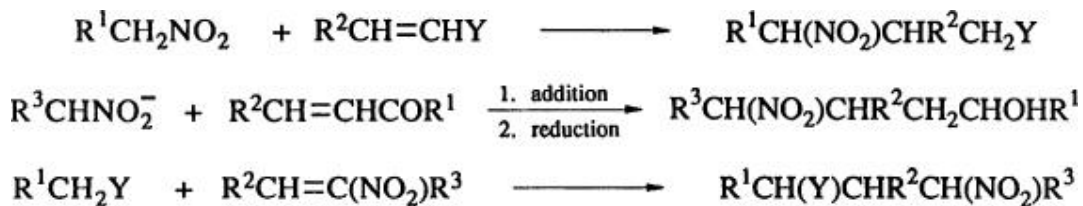
Many reactions of nitro compounds reflect the equilibrium with nitronic acids **1** (also called *aci*-nitro or isonitro compounds). (31) These nitronic acids



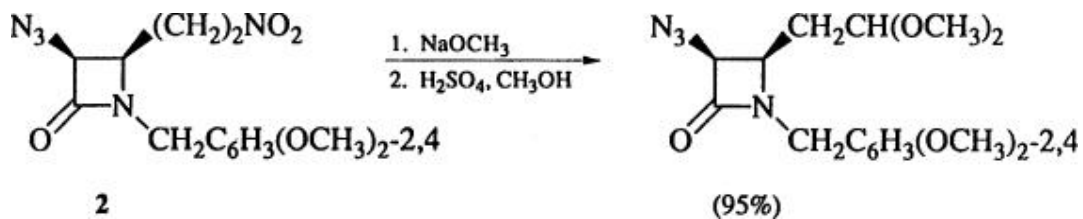
are much like enol forms of ketones—they are much more acidic than nitro compounds (2–5 pK_{a} units), (32) and the equilibrium lies very much on the side of the nitro isomer. Typical values for the equilibrium constant K_{eq} are 10^{-5} to 10^{-7} . 3a

Nitronate salts are formed by treating nitro compounds with any aqueous alkali. Water-miscible cosolvents such as dioxane, tetrahydrofuran (THF), or alcohols can also be used, particularly when the nitro compound has limited solubility in water. For example, treatment of nitro compounds with sodium methoxide in methanol gives acetals after addition of acid from even large primary nitroparaffins. (33) Stronger bases are used in aprotic media. As an illustration, nitronates from primary nitro compounds can be deprotonated by using *n*-butyllithium as the base in an aprotic solvent like tetrahydrofuran. (6)

A wide range of substituted nitro compounds undergoes the Nef reaction. These include γ -nitroketones, (34) γ -nitroalcohols, (35) γ -nitroesters, (36, 37) and γ -nitro nitriles. (38, 39) All of these are available by Michael reactions. α -Keto



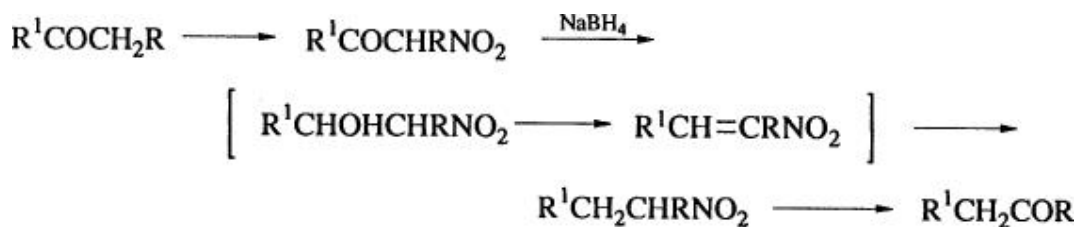
aldehydes are available from α -nitroketones. (40) α -Hydroxy aldehydes and ketones are isolated from the condensation of nitro compounds with aldehydes followed by a Nef reaction. Many examples of this chemistry are found in the carbohydrate field as early as 1944. (41) Aldoses are often used in condensation reactions with nitroparaffins to give highly functionalized nitro compounds which undergo the Nef reaction. An α -acetamidoaldose can also be prepared in this way. (42) Other polyfunctional compounds that undergo the Nef reaction include the azido- β -lactam **2**. (43)



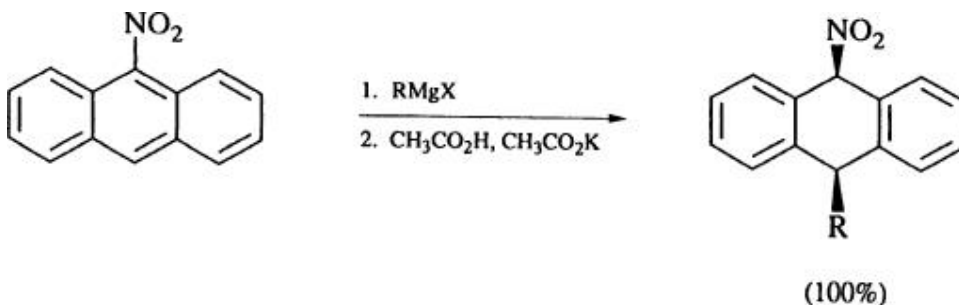
The Nef reaction has been used as the key step in a 1,2 transposition of carbonyl groups (p. 660). (44) Thus a ketone is nitrated at the alpha position with a nitrate ester, (24, 25) and the carbonyl group is reduced with sodium borohydride. Loss of water followed by conjugate reduction with sodium borohydride gives a nitro compound which is then submitted to the Nef

reaction. Unfortunately, since reduction of some nitroolefins is incomplete, a reductive Nef process using zinc is necessary in order to obtain clean results.

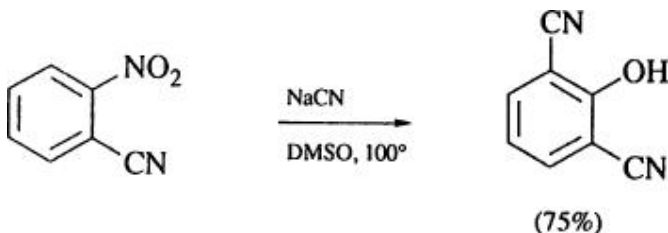
Some aromatic nitro compounds undergo addition of nucleophiles to give nitronate anions which can be protonated to give either the nitro compound



or the Nef product. (45-48) For example, addition of a Grignard reagent to 9-nitroanthracene followed by workup with buffered acetic acid gives the *cis* adduct. (45) Similar results are obtained with nitronaphthalenes. (46) The Nef process is observed in the reaction of *o*-nitrobenzotrile with sodium cyanide



where 2,6-dicyanophenol is obtained in 60–75% yield. (47, 48)



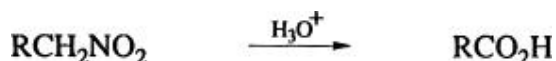
3.2. Side Reactions That Complicate the Nef Reaction

Nitronates are reactive toward electrophiles at several sites because of delocalization of the negative charge, and this often leads to complications. Addition of a proton to the alpha carbon atom regenerates the nitro compound, (1, 49) whereas the desired Nef process requires protonation on one of the oxygen atoms to give a nitronic acid. More stable nitronates tend to give the

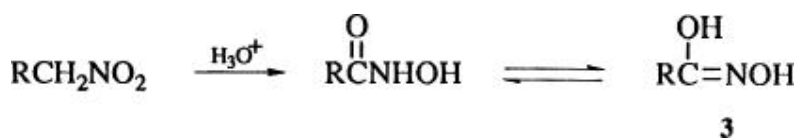
nitro compounds upon acidification. (20, 49) This regeneration of nitroparaffins is the only reaction if mild acids capable of destroying nitrous acid (like hydroxylamine hydrochloride or urea and acetic acid) are used. (20)

Another problem arises as a result of nitrite ion behaving as a good leaving group. Many nitro compounds eliminate upon treatment with base. This is a problem particularly when the nitro group is beta to an acidifying functionality like a carbonyl group. While this is a side reaction for the Nef reaction, it can have synthetic utility. 3d

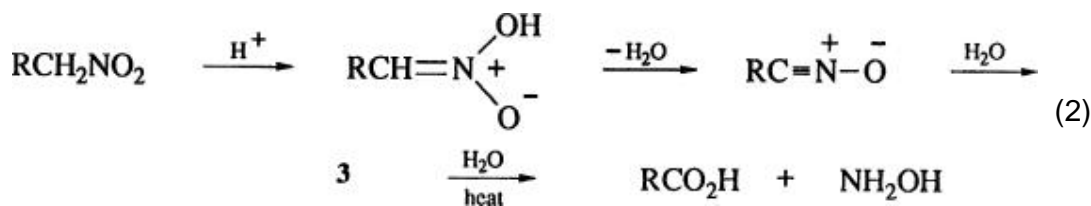
As mentioned above, acid itself can cause reactions other than the Nef reaction although the product may be identical. There is one report of the direct conversion of a nitro compound into a ketone by treatment with acid. (50) Thus 2-nitrooctane gives 2-octanone after prolonged reflux with 1 N hydrochloric acid in a heterogeneous system. The conversion is only 35% complete after nearly 2 weeks of heating. The action of strong acid on nitro compounds was discovered by Meyer 11 years before Nef recorded his initial observations. (51) In the Meyer reaction, primary nitro compounds are converted into carboxylic acids by treatment with hydrochloric acid or sulfuric acid. (51-59) This



process involves hydroxamic acids 3 as intermediates, (19, 59-61) which are usually

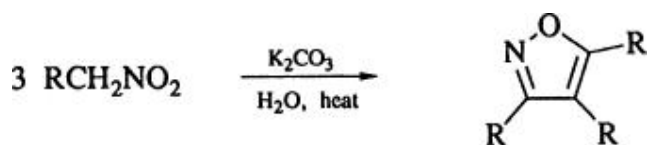


isolated simply by avoiding heat. (15, 60-65) The mechanism of the Meyer reaction is shown in Eq. 2. (15, 61, 63-65) A thorough study of the kinetics indicates that the reaction proceeds at a maximum rate at a pH less than that required to protonate all of the neutral nitronic acid. (64, 65) This suggests that a competitive reaction takes place involving O-protonation of the nitronic acid, followed by loss of water and a proton to give the nitrile oxide. (65) The nitrile oxide has been trapped by 1,3-dipolar cycloaddition to alkenes and alkynes. (66)

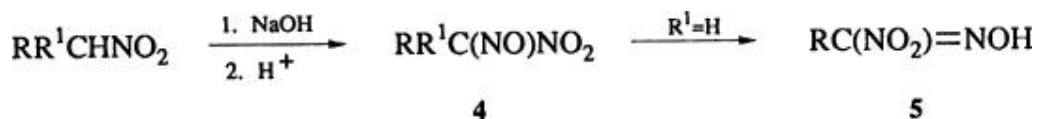


Several reports indicate that nitronate salts derived from primary nitro compounds give carboxylic acids upon acidification. (62, 67, 68) Although these seem to be abnormal Nef reactions, undoubtedly the Meyer reaction is the true pathway because of the strong acid or vigorous conditions employed. Direct acidification of 1-phenylnitroethane and 1-phenylnitropropane in the presence of potassium nitrite gives acetophenone and propiophenone, respectively. (69)

Nitroalkanes sometimes undergo self-condensation upon exposure to base. As might be expected, this process is a serious problem with less-hindered nitro compounds such as nitromethane, which readily forms methazonate ion ($^-\text{O}_2\text{N} = \text{CHCH} = \text{NO}^-$) upon treatment with hydroxide ion. (70, 71) In addition, small primary nitroparaffins (nitroethane, 1-nitropropane, and 1-nitrobutane) undergo trimerization in the presence of even weak bases such as triethylamine or potassium carbonate to give isoxazoles. (72, 73) This conversion proceeds via the aldehyde, which condenses with the nitroalkane. (72)



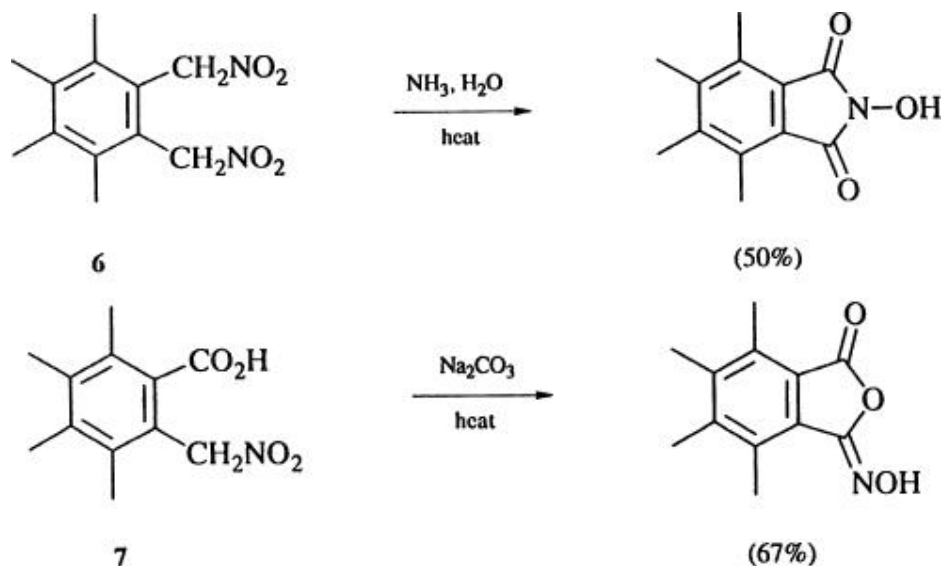
Another side reaction that complicates the Nef reaction is the formation of pseudonitroles **4** from secondary nitro compounds and nitrolic acids **5** when primary nitroalkanes are used. (74-76) These products are favored by slow



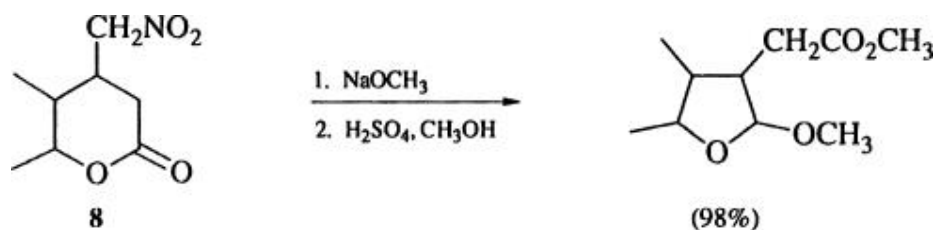
addition of the nitronate to acid. (75) Since nitrous acid is the cause of the nitrosation, addition of a good nitrous acid scavenger such as urea prevents

this problem. (1, 20)

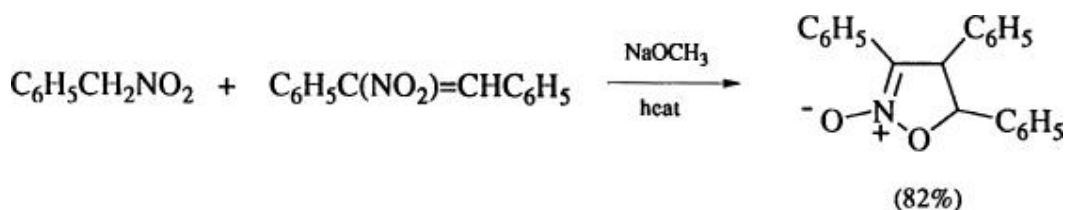
Certain polyfunctional molecules can lead to undesired products because of interaction of neighboring groups or loss of some functionality under the reaction conditions. Attempted Nef reactions on the dinitro compound **6** (77) or nitro acid **7** (78) lead mainly to heterocyclic products, presumably via the



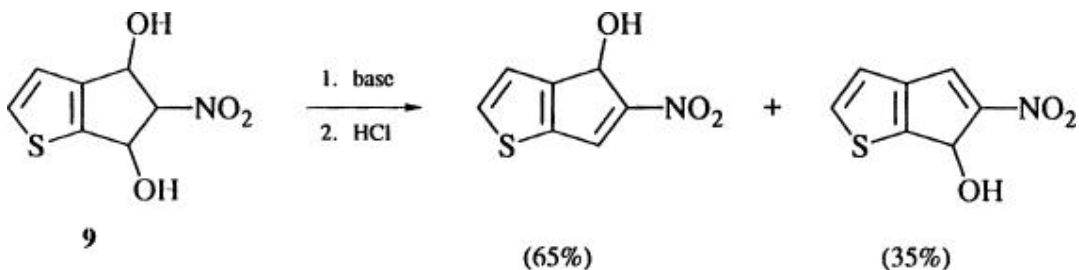
corresponding nitronic acids. The nitro lactone **8** undergoes ring opening as well as the Nef reaction and gives an unexpected acetal. (79) Loss of nitrite ion



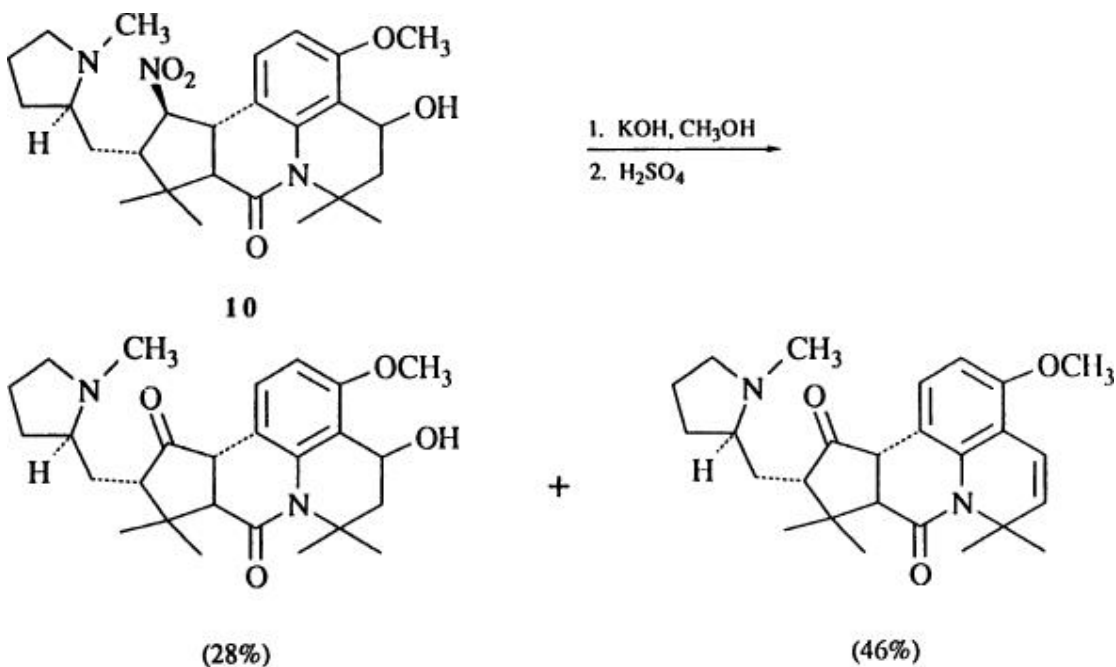
by intramolecular displacement occurs faster than acidification and complicates the reaction of α -nitrotoluene with α -nitrostilbene. (80) The strong acid



used in the Nef reaction causes dehydration of compound **9** instead of the

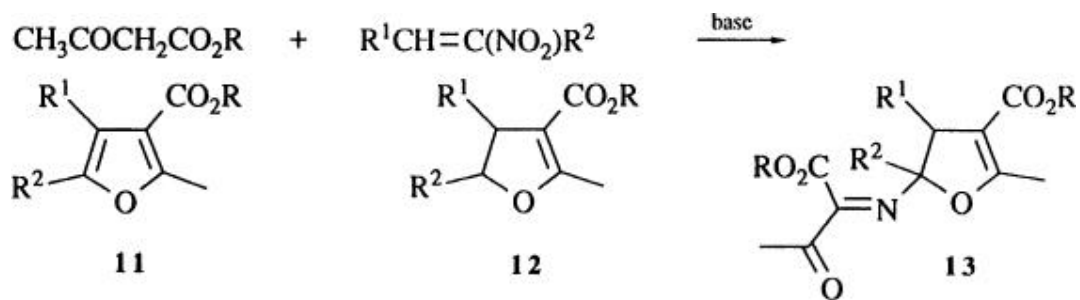


Nef reaction, (**81**) and leads to partial dehydration as a byproduct from nitro compound **10**. (**82**)



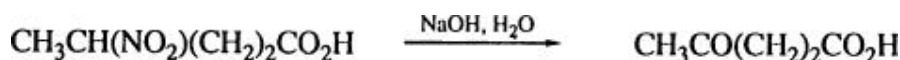
2-Nitro-1-butanol gives mixtures of the Nef product (1-hydroxy-2-butanone) and 2-nitro-1-butene as well as some of the oxime of the Nef product. (**83**) These competing reactions are pH-dependent. The Nef process is favored at high acidity (pH 1.1 is best). (**83**)

γ -Nitroketones derived from the addition of β -keto esters to nitroolefins undergo intramolecular reactions in the presence of alcoholic sodium or potassium hydroxide and attempted Nef reaction with acid to give furans **11**, **12**, or **13**. (**84-87b**) In contrast, the presence of a neighboring carboxylate

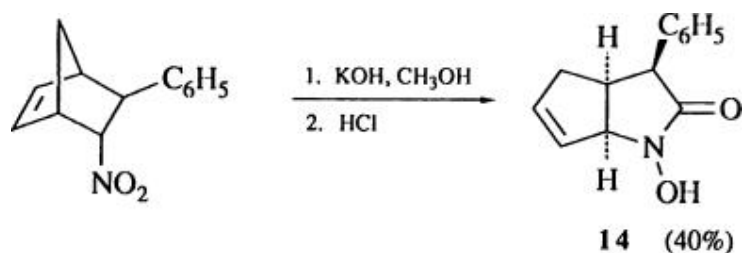


R	R ¹	R ²			
C ₂ H ₅	C ₆ H ₅	C ₆ H ₅	(72%)	—	—
C ₂ H ₅	4-ClC ₆ H ₄	C ₆ H ₅	(3%)	(14%)	—
CH ₃	2,4-Cl ₂ C ₆ H ₃	CH ₃	—	—	(70%)

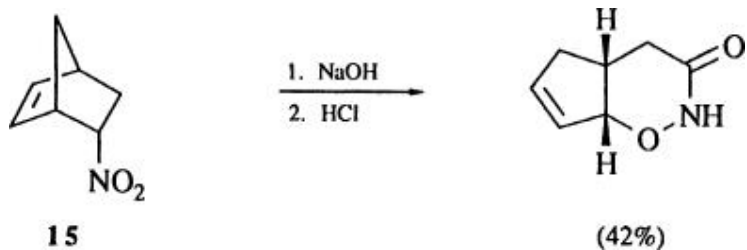
group causes an accelerated Nef reaction with 4-nitrovaleric acid, possibly by intramolecular protonation. (88)



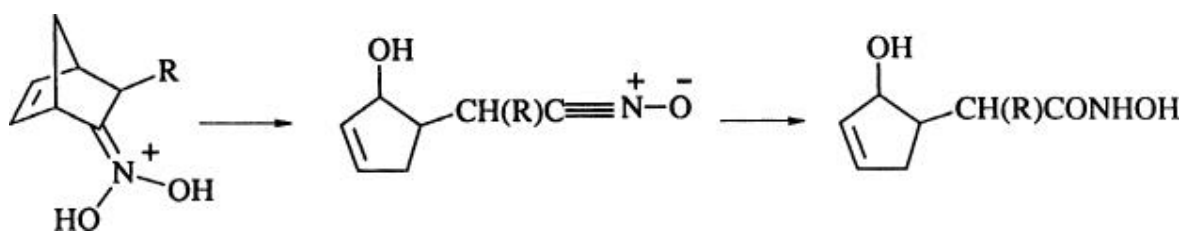
Rearrangements also occur under Nef reaction conditions if the substrates are prone to form carbocations, for example, those containing the bicyclo[2.2.1]heptane skeleton. An attempt to carry out the Nef reaction with 5-nitro-6-phenylbicyclo[2.2.1]hept-2-ene was not successful. (89) The structure of the rearrangement product was subsequently shown to be *N*-hydroxylactam **14**. (90) A similar reaction occurs when the phenyl group is replaced with a



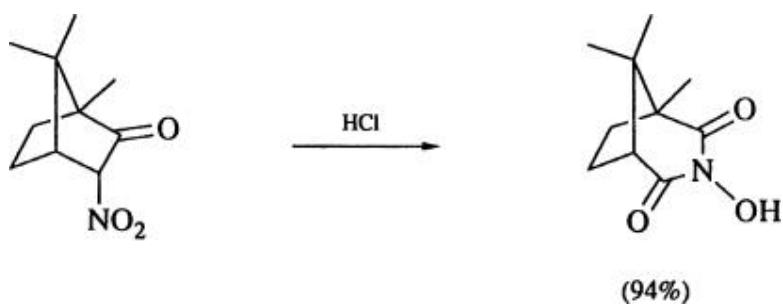
methyl group. (90) The rearrangement products from very similar compounds (91-93) such as **15** (91) are of a different structural type. Both of these products arise



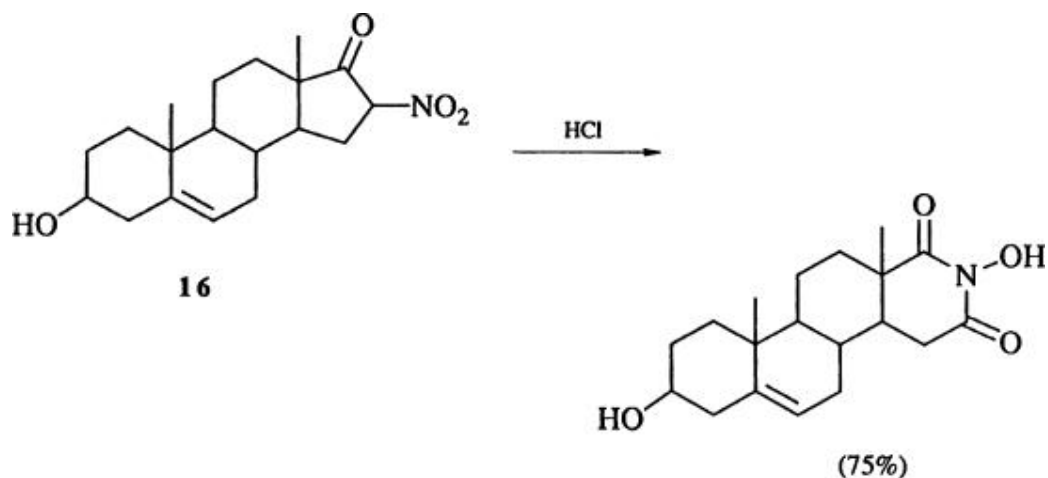
by ring opening of the *aci*-nitro compound to give a nitrile oxide and then a hydroxamic acid, which can form a ring via attack by either oxygen or nitrogen. (90, 91)



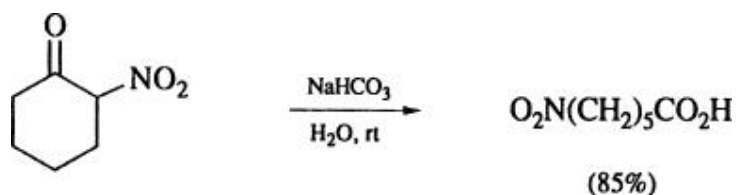
α -Nitrocamphor as well as the corresponding nitronate give an *N*-hydroxymide upon exposure to hydrochloric acid by a similar mechanism. (94, 95)



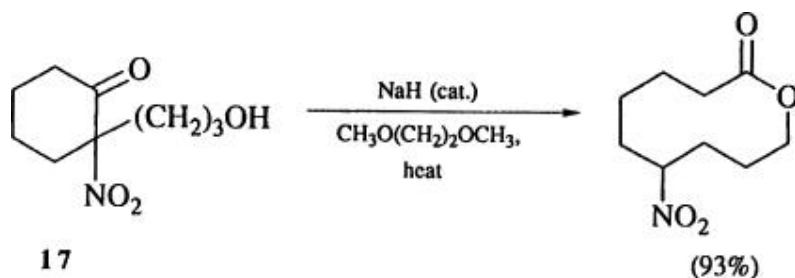
A similar reaction occurs with the nitrosteroid **16**. (96) Many cyclic α -nitro



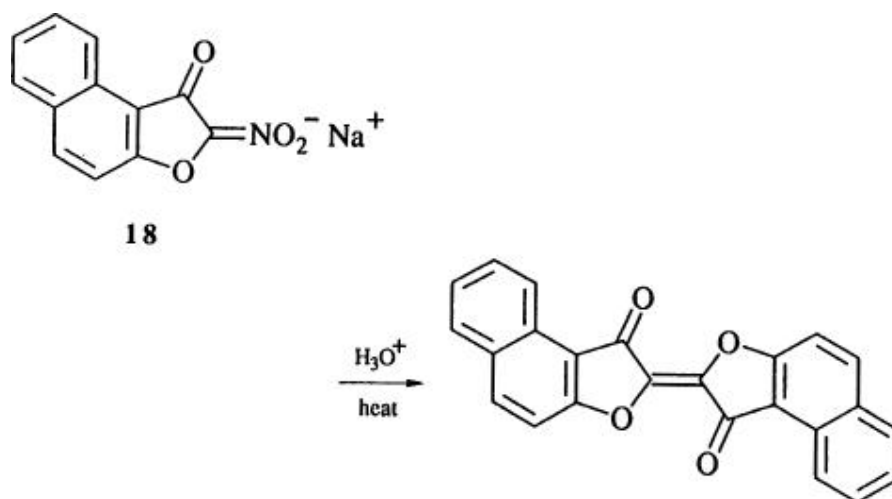
ketones undergo this type of rearrangement under acidic conditions; however, exposure to nucleophiles like water or alcohols under either acidic or basic conditions gives the ring-opened nitro acid or ester by way of a retro aldol reaction. (24, 97, 98)



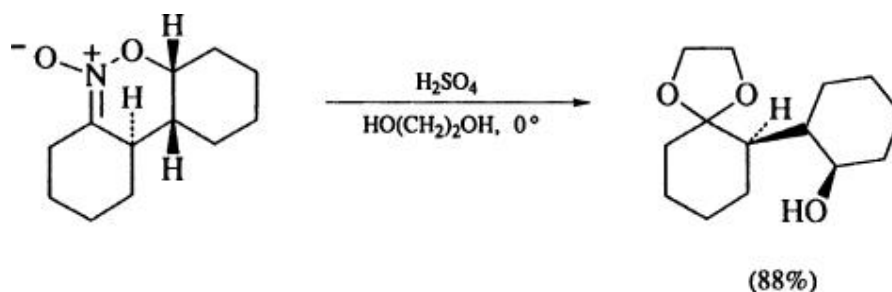
An interesting modification is the intramolecular variant of this reaction, which can be used to prepare macrocyclic nitro compounds. (99-103) For example, a 10-membered ring nitro lactone is produced by reacting the substituted nitrocyclohexanone **17** with a catalytic amount of sodium hydride in hot 1,2-dimethoxyethane. (99) Such cyclic nitro compounds can then be subjected to the Nef reaction to yield ketolactones or keto diacids.



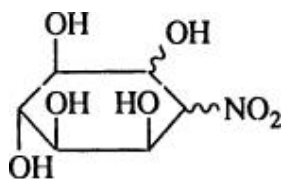
The salt of α -nitro ketone **18** dimerizes when exposed to acid. (104, 105)



Some Nef products are prone to undergo epimerization. A nitronic ester is obtained by cycloaddition of 1-nitrocyclohexene to cyclohexene and is sensitive to loss of optical activity under the usual Nef conditions with sulfuric acid and water. (106) When the reaction is carried out in the presence of ethylene glycol at 0° , no epimerization is observed in the isolated hydroxyketal. (106)

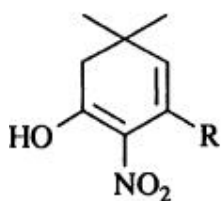


Some nitro compounds fail to react under Nef conditions. For example, the nitrodeoxyinositol mixture **19** is recovered unchanged from an attempted Nef reaction using barium hydroxide followed by sulfuric acid. (107, 108) A variety



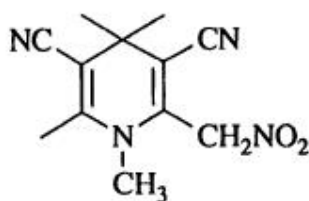
19

of fluorinated nitro compounds also fail to give Nef reaction products, although no experimental details are available. (109) It is possible that these reactions fail because the nitronate anions are not formed completely. Use of a stronger base or modified Nef conditions might be helpful. Other systems fail to undergo the Nef reaction because the corresponding nitronate salts are highly stabilized and tend to protonate on carbon rather than oxygen. (20, 49) Examples are the nitro compounds **20** (110, 111) and the heterocycle **21**. (112) The benzylic nitro compound **22** (113) also fails to give useful amounts of Nef product, possibly for the same reason. Another system that does not undergo the Nef reaction is nitro compound **23**, (114) in which only starting material is recovered

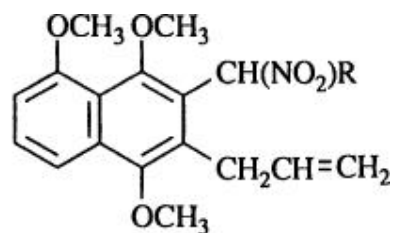


20

R=H, CH₃

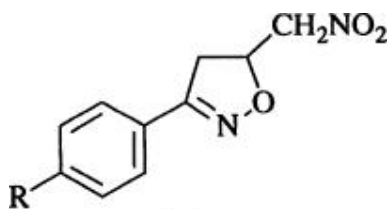


21



22

after exposure to sodium ethoxide at -15° followed by sulfuric acid. The use



23

R=H, NO₂

of bromine instead of sulfuric acid gives the α -bromonitro compound, showing that the nitronate was formed. This result seems to rule out elimination to the nitroolefin, although acidification of the nitroolefin could give **23** by conjugate addition of an oximino nitroalkene intermediate, and bromination of the nitroolefin could yield the α -bromo compound via a bromonium ion.

3.3. Modified Nef Reactions

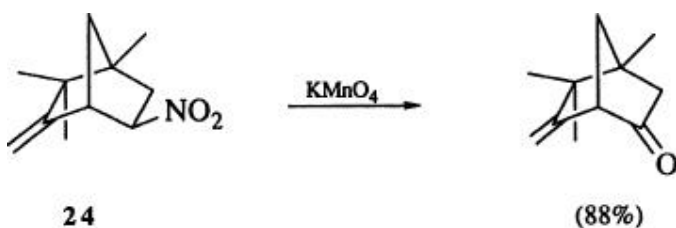
Considerable effort has been directed toward the development of modified Nef reaction conditions for several reasons. First, some compounds are prone to undergo side reactions or fail to react as discussed in the preceding section. Second, the use of base followed by acid, as in the traditional Nef reaction, is incompatible with many polyfunctional molecules. Thus, the scope of the Nef reaction has been widened considerably by the use of modified methods to accomplish this conversion. Many of the modified approaches utilize oxidizing agents or reducing agents. Each method is discussed, and specific examples are provided in the tables.

3.3.1.1. Oxidizing Agents

Numerous reagents accomplish the Nef conversion by way of an oxidation. These are discussed individually roughly in the order of their discovery, but with some consideration for synthetic utility as well.

3.3.1.2.1. Potassium Permanganate

One of the modified Nef reactions, discovered in the early 1900s, (115-123) uses potassium permanganate to cleave the nitronate salts of various compounds. The yields range from 12–100% when applied to simple nitro compounds or unsaturated bicyclic nitro compounds like **24**.

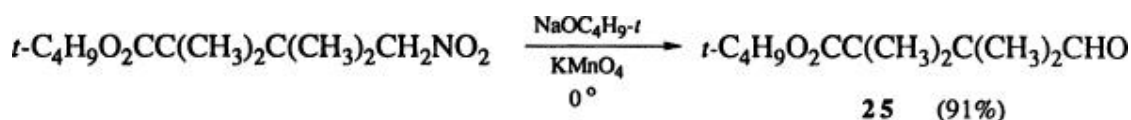


It is significant that the nitronate oxidation is faster than the cleavage of alkene double bonds. This reaction was reinvestigated in 1962 and it was found to proceed with higher yields than the “normal” Nef reaction. (124) In addition, aldehydes can be isolated when excess potassium permanganate is avoided. (124-131)

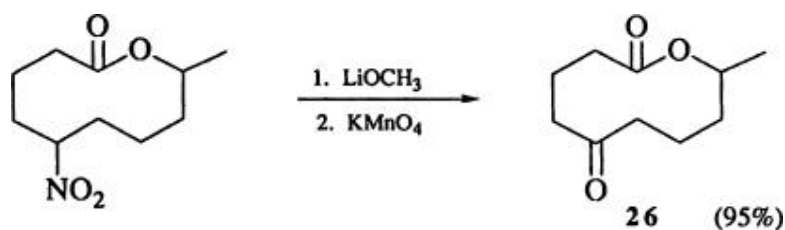
Carboxylic acids are obtained from primary nitroparaffins when excess reagent is used (greater than 0.67 equivalent). (124, 129-132) The reaction usually is carried out in a medium buffered with magnesium sulfate or a borate salt. Analysis of the kinetics suggests that the key step is attack of permanganate ion on the $\text{C} = \text{N}$ bond of the nitronate salt. (133-135)

The original procedure involves the use of potassium hydroxide for the formation of the nitronate salts, but this sometimes leads to erratic results. This problem can be overcome by using sodium hydride in *tert*-butyl alcohol and

pentane. (126, 127) Under these conditions, addition of aqueous potassium permanganate leads to 59–96% isolated yields of aldehydes such as **25**. (126, 127)



Lithium methoxide followed by potassium permanganate gives a 95% yield of the ketolactone **26**. (99) An analogous ketolactam can be prepared by the same general procedure. (136)

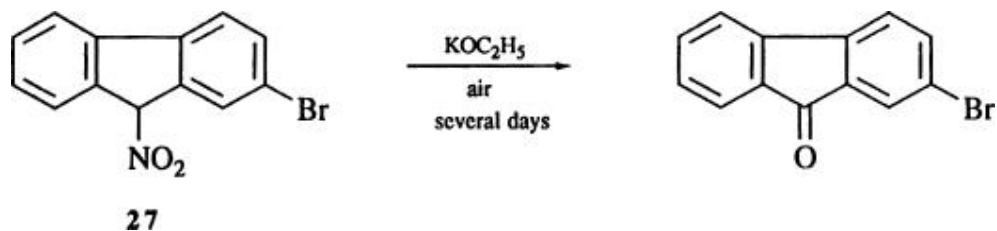


Cetyltrimethylammonium permanganate in methylene chloride converts numerous nitro compounds into aldehydes and ketones at room temperature in good yields. (136a) For example, camphor is isolated in 65% yield and heptanal in 71% yield.

See also the section on silica-gel supported potassium permanganate reactions for further examples (p. 680).

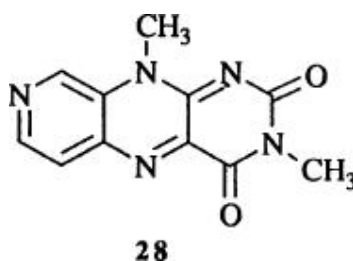
3.3.1.2.2. Oxygen and Ozone

The conversion of nitro compound **27** into the corresponding



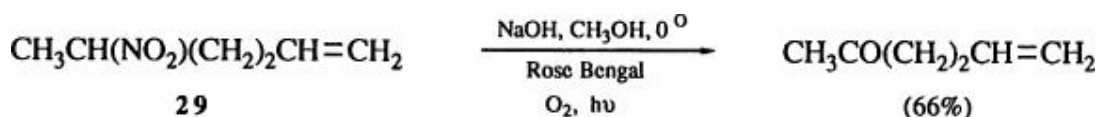
ketone in unspecified yield by treatment with potassium ethoxide and then exposure to air was reported 50 years ago. (137) This type of reaction was studied 20 years later and found to represent an autoxidation. (138) Thus 2-nitropropane is converted into acetone and nitrite ion by exposure to sodium

hydroxide and air. More recently, the 8-azaflavin **28** has been found to catalyze

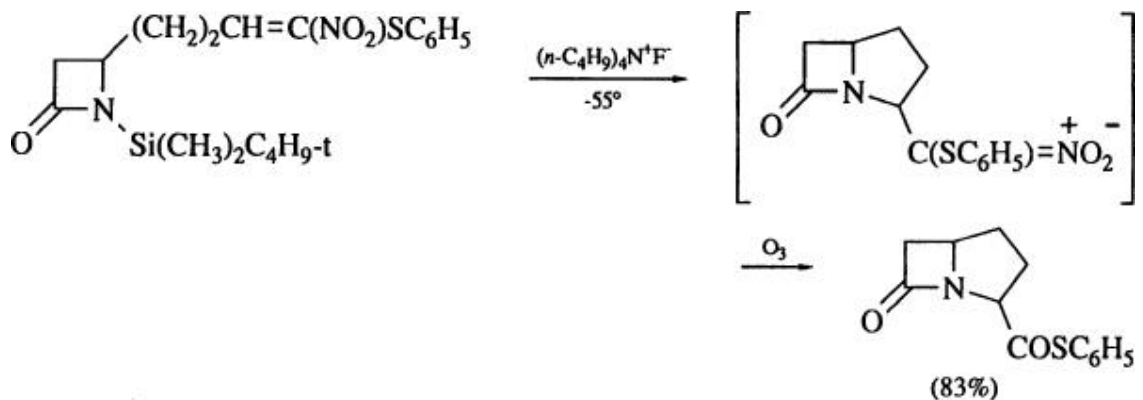


this reaction. (139) The oxidation of nitronates with molecular oxygen appears not to have much synthetic utility unless inexpensive catalysts can be found. Ferric chloride accelerates the formation of acetone, (138) but the scope and possible synthetic applications have not been studied.

Singlet oxygen also converts nitronate salts into aldehydes and ketones. (140) Thus irradiation of basic solutions of four different nitro compounds in the presence of oxygen and Rose Bengal gives the corresponding carbonyl compounds in 49–67% yield. This group includes nitroalkenes such as compound **29**.

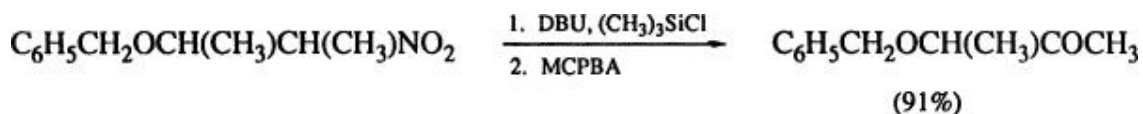


Ozone also accomplishes this Nef-like reaction. Nitro compounds can be deprotonated with sodium methoxide in methanol and then exposed to ozone at -78° . Workup with dimethyl sulfide gives the carbonyl compounds in 65–88% yields. (141, 142) Aldehydes may also be obtained without difficulty. Functional groups that are unaffected include ketone carbonyl, ester, and ketal. (140) Thioesters can be obtained by ozonolysis of a nitronate generated by a conjugate addition. 143,143a



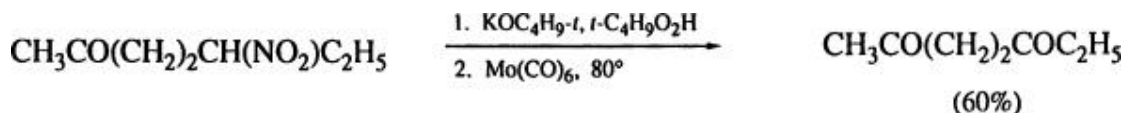
3.3.1.2.3. *m*-Chloroperoxybenzoic Acid

Trialkylsilyl nitronates are formed from secondary nitro compounds, base (e.g., 1,8-diazabicyclo[5.4.0]undec-2-ene, DBU), and chlorosilanes. These nitronate esters react with *m*-chloroperoxybenzoic acid (MCPBA) to give ketones in 70–99% yields. (143b) β -Substituted nitro compound substrates can be prepared from the corresponding nitro-olefins. (143b)



3.3.1.2.4. *tert*-Butyl Hydroperoxide/Oxovanadium(IV) Bisacetylacetonate or Molybdenum Hexacarbonyl

tert-Butyl hydroperoxide converts nitronate salts into aldehydes or ketones in the presence of oxovanadium(IV) bisacetylacetonate or molybdenum hexacarbonyl as a catalyst. (144) Ketals, acetals, and alkenes survive the reaction. Unfortunately, most of the published examples of this reaction give yields determined only by gas chromatography. A slight excess of the hydroperoxide leads to overoxidation of primary nitro compounds, and systems containing ketone or ester groups require refluxing benzene and molybdenum hexacarbonyl as a catalyst. (144) Furthermore, water appears to inhibit the reaction so that 90–100% *tert*-butyl hydroperoxide is required. (145)



3.3.1.2.5. Oxodiperoxomolybdenum(VI)/Pyridine/Hexamethylphosphoric triamide

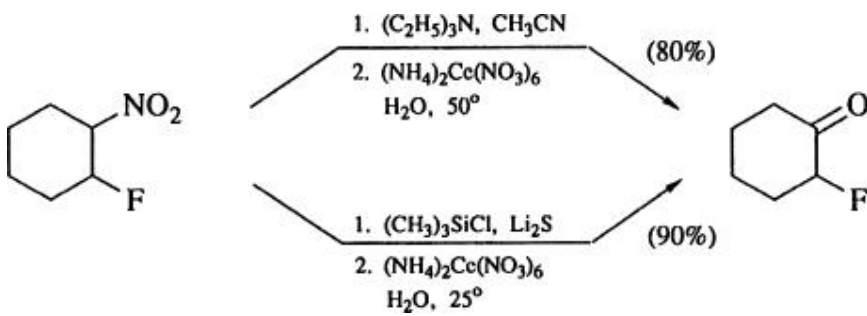
The salts of secondary nitro compounds are converted into ketones by the pyridine/hexamethylphosphoric triamide (HMPA) complex of molybdenum(VI) peroxide. (145) Since this reagent is known to effect hydroxylations of carbanions, it is assumed that the reaction proceeds via an intermediate α -nitroalcohol, which then loses nitrous acid. Nitronates from primary nitro compounds yield carboxylic acids instead of aldehydes as a result of rapid oxidation of the latter under the reaction conditions. The nitronate salts can be formed with either lithium diisopropylamide (LDA) or triethylamine. Ester groups and activated benzylic positions are tolerated. Ethyl pyruvate is obtained from ethyl 2-nitropropanoate in 73% yield.

3.3.1.2.6. Hydrogen Peroxide

Another modified Nef reaction uses mild reaction conditions. The nitro compound is stirred at room temperature with 30% hydrogen peroxide and potassium carbonate in methanol followed by acidification with dilute hydrochloric acid. (146, 147) Isolated yields of both aldehydes and ketones are 76–96%. (147) For example, hexanal is isolated in 80% yield, while an 88% yield of cyclohexanone is obtained. (147) The combination of mild conditions and high yields makes this a very attractive alternative to the Nef reaction. Numerous other functional groups should survive under these conditions, although this has not been confirmed.

3.3.1.2.7. Ceric Ammonium Nitrate (CAN)

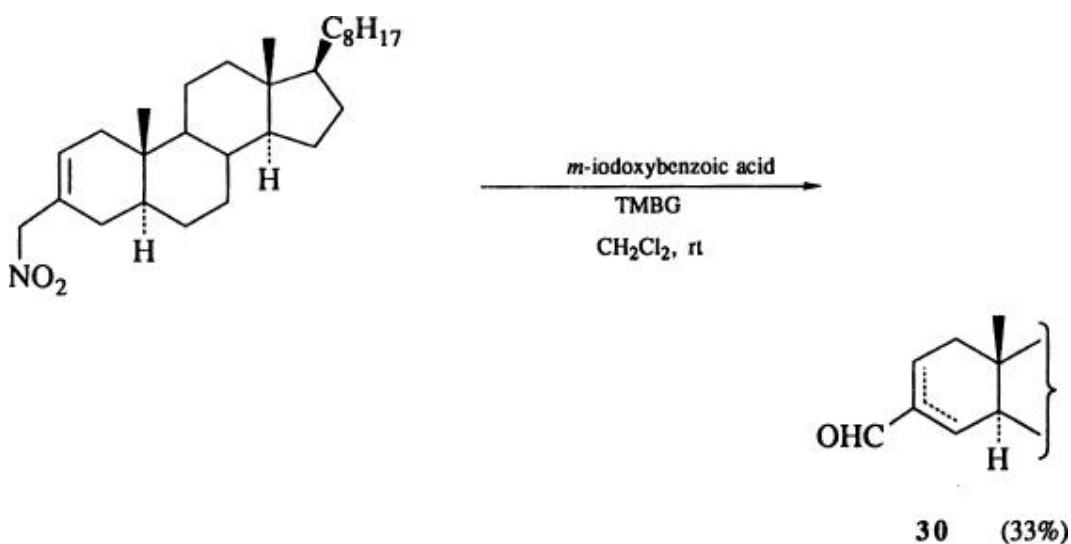
High yields of aldehydes and ketones can be obtained by stirring nitro compounds with triethylamine and ceric ammonium nitrate [ammonium cerium(IV) nitrate] in aqueous acetonitrile at 50°. (148) The carbonyl compounds are isolated in 67–85% yields. Initial conversion of the nitro compound into the *O*-trimethylsilyl nitronate with trimethylsilyl chloride and lithium sulfide permits the ceric ammonium nitrate step to proceed at room temperature in only 5 minutes with 90–92% yields of ketones being realized. 2-Fluorocyclohexanone is the only ketone produced by this method that contains any functional group.



3.3.1.2.8. *m*-Iodoxybenzoic

Acid/*N,N,N,N*-Tetramethyl-*N'*-*tert*-butylguanidine

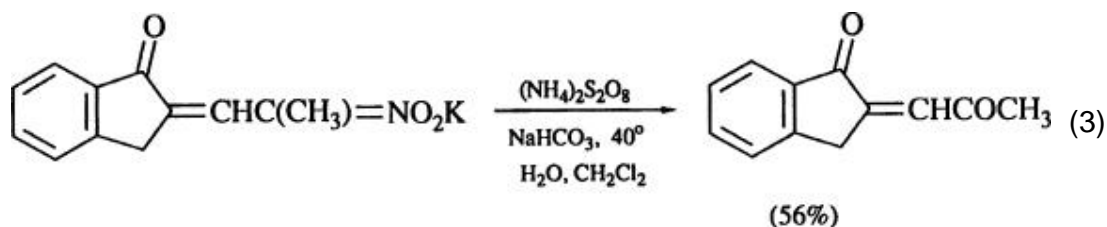
A wide range of functional groups including esters, ketones, dithioketals, alkenes, and alcohols are inert to *m*-iodoxybenzoic acid and the weak base *N,N,N,N*-tetramethyl-*N'*-*tert*-butylguanidine (TMBG); the nitro groups of several nitrosteroids are converted into carbonyl groups by this reagent combination in 33–95% yields. (149) 1,2-Diols also cleave readily. The only reported example of a primary nitro compound is an allylic system which gives the mixture of aldehydes **30** in 33% yield, isolated as the 2,4-dinitrophenylhydrazones. (149)



The reaction causes the double bond to isomerize in this system so that both compounds are formed.

3.3.1.2.9. Other Inorganic Salts

Several inorganic salts can be used to obtain vicinal dinitro compounds by the oxidative dimerization of nitronate salts, although the corresponding carbonyl compounds are also formed. (146, 150) For example, ammonium or sodium persulfate converts the anion of 2-nitrobutane into 2-butanone (48%) and 3,4-dimethyl-3,4-dinitrohexane (37%). (146) Aldehydes can be obtained in low yields (27–38%), although benzaldehyde is obtained in 75% yield. Only ketones are obtained from highly conjugated nitronates (Eq. 3). (151, 152) Stirring 2-nitropropane with cupric chloride and ammonium hydroxide



in aqueous sodium hydroxide gives acetone in 75–90% yield. (146) No other examples of this reagent combination are reported. Low yields of acetone (25–30%) are obtained from the exposure of 2-nitropropane and sodium hydroxide to silver nitrate. (146) Fluorenone is obtained in 33% yield from 9-nitrofluorene by this method. (150) Acetone is isolated in 55% yield as the 2,4-dinitrophenylhydrazone when 2-nitropropane is combined with sodium hydroxide and potassium ferricyanide. (147) Sodium bromate gives an unreported amount of acetone from sodium 2-propanenitronate. (146)

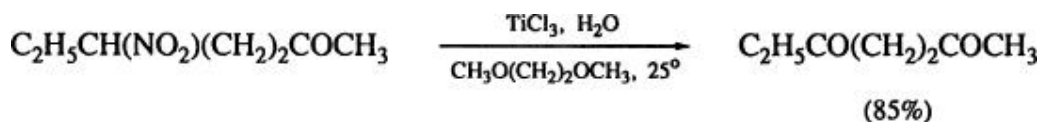
In summary, only persulfate ion seems to be of any synthetic value for the preparation of ketones.

3.3.1.3. Reducing Agents

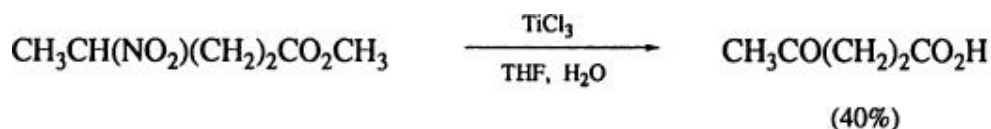
Only a small number of reagents convert nitro compounds into the corresponding aldehydes and ketones by a reductive process. Nonetheless, this is an important extension of the Nef reaction. Five reagents are discussed with the most significant method mentioned first. It is assumed that most of these processes involve oximes as intermediates; indeed, several methods give oximes as isolable products which can be hydrolyzed to complete this reductive alternative to the Nef reaction. Finally, in electrolysis, the reducing electrons are obtained from an electrical source rather than a chemical one.

3.3.1.3.1. Titanium Trichloride

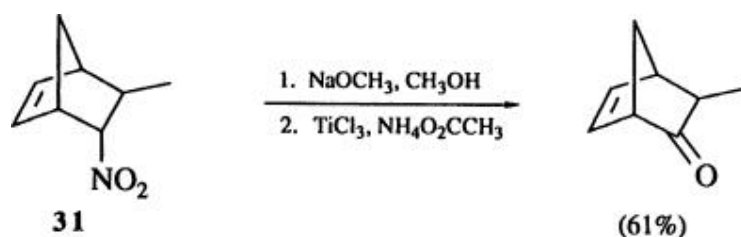
The most widely used reductive modified Nef reaction uses freshly prepared aqueous titanium trichloride. (153) The reactivity of this reagent requires manipulation under an inert atmosphere. The reducing agent can be stored over zinc for prolonged periods of time. (153) Unfortunately, aqueous titanium trichloride is very acidic (pH < 1) so that esters may suffer



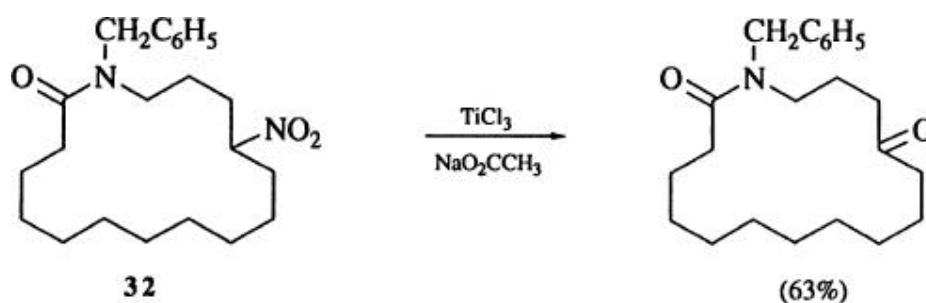
hydrolysis, carbon–carbon double bonds may isomerize, and ketals are deprotected. (154) 2-Methyl-2-nitropropane is cleaved to acetone with hot titanium trichloride. (155) The use of an ammonium acetate or sodium acetate buffer allows



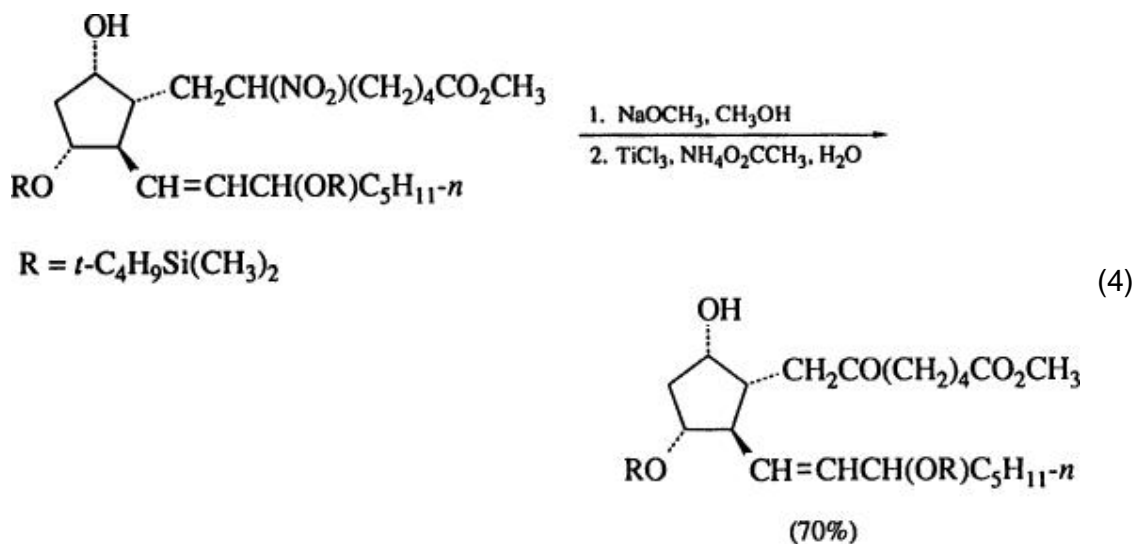
the reaction to proceed at pH 5–6 with the survival of these functional groups. (99, 136, 154-160) Under these conditions, the reaction is successful even with systems prone to acid-catalyzed rearrangements, such as compound **31**. (161)



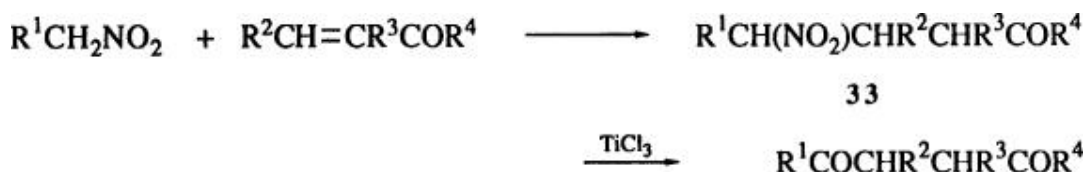
Aldehydes can be prepared from some nitrosteroids (154, 162) that do not undergo the conventional Nef reaction. (163) This method also succeeds in some cases that do not work well with an oxidative Nef method, such as compound **32**. The latter fails to give the corresponding ketone with buffered potassium permanganate. (136)



Compounds containing several functional groups also undergo the desired reaction (Eq. 4). (160) This example illustrates that the nitronate anion is often formed prior to addition of the buffered titanium salt, although there are examples where the nitronate salt is not preformed. (158, 161)

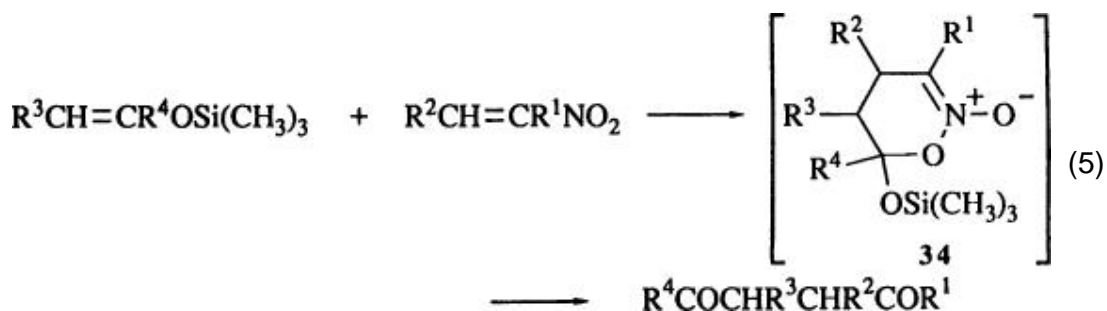


A useful synthetic application of the Nef reaction is the generation of a 1,4-dicarbonyl compound from an α, β -unsaturated carbonyl precursor via the nitro compound **33**. Titanium trichloride is used for the modified Nef reaction

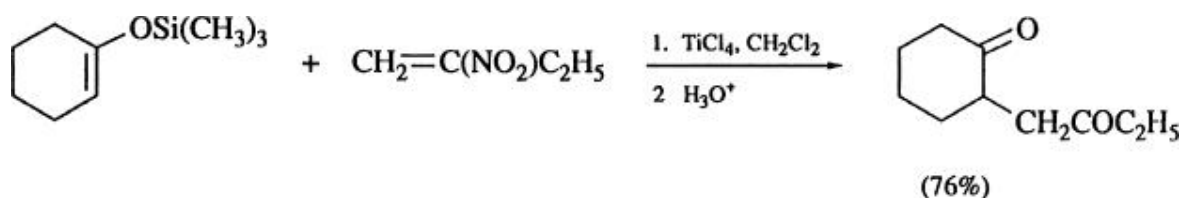


step of this sequence. (153, 154) For example, 1-nitropropane reacts with methyl vinyl ketone in the presence of diisopropylamine to give 5-nitro-2-heptanone in 55% yield. Treatment of the latter with titanium trichloride gives 2,5-heptadione in 85% yield. (154)

An alternative preparation of nitro compound **33** by using Lewis acids to catalyze the reaction of enol silyl ethers with nitroolefins is an even more convenient synthetic procedure because it is often a one-pot operation. (164-168) The Lewis acids used are often titanium tetrachloride and stannic chloride; aluminum chloride has been used occasionally. An *O*-silyl species **34** is assumed to be an intermediate (Eq. 5). Recently, the intermediate **34** was



isolated, examined spectroscopically, and purified when dichlorodiisopropoxytitanium was used as the catalyst. (169) Hydrolysis of **34** to the 1,4-dicarbonyl compound is easy and is quantitative when titanium tetrachloride, stannic chloride, or aluminum chloride is used. (164-168) A change in stereoselectivity in



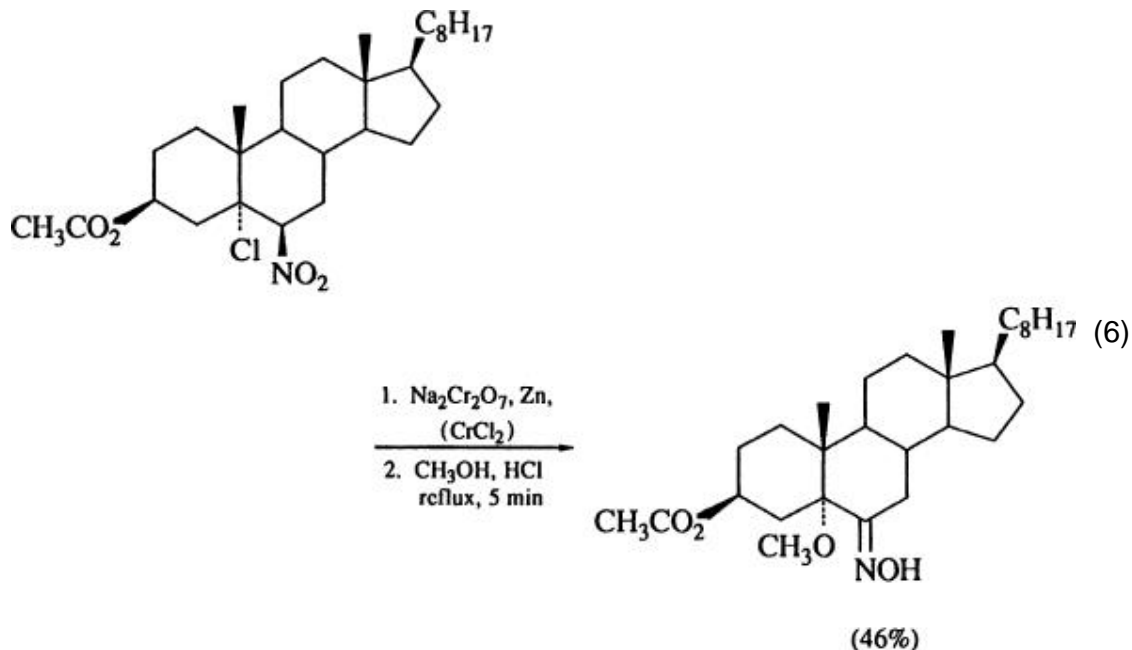
the nitro ketone **33** is observed in some systems when dichlorodiisopropoxytitanium is used as the catalyst. (169)

3.3.1.3.2. Vanadium(II) Chloride

Simple ketones and aldehydes can be isolated in 24–71% yields by stirring nitro compounds with vanadium(II) chloride, aqueous hydrochloric acid, and dimethylformamide. (170) The pH is so low that acid-sensitive functionalities cannot survive. In fact, octanal is obtained from 1-nitrooctane in only 24% yield because of a competing aldol reaction.

3.3.1.3.3. Chromium(II) Chloride

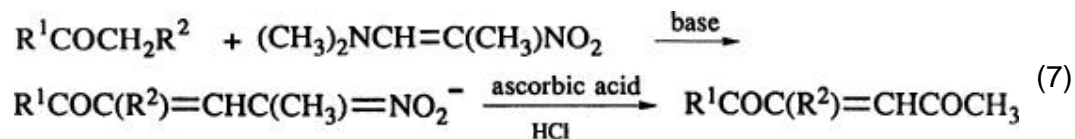
Nitro compounds are converted by chromium(II) chloride (171) and aqueous hydrochloric acid in hot methanol into the corresponding aldehydes and ketones in 32–77% yields, isolated as 2,4-dinitrophenylhydrazones. (172) Since this reagent reduces nitrobenzenes and sulfoxides as well, another reducible functionality cannot be present. Oximes are obtained by combining steroidal nitro compounds with chromium(II) chloride with a brief reflux period (Eq. 6) (173) or at room temperature. (174) Chromium(II) chloride



is unstable and has to be generated in situ as in Eq. 6.

3.3.1.3.4. Ascorbic Acid

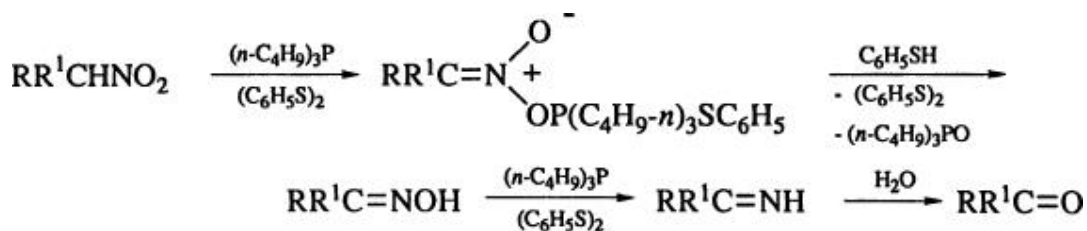
Another reductive method uses ascorbic acid to transform stabilized nitronate salts into the corresponding ketones. (152) Thus diketones are obtained in 8–37% yields from nitro enamines and ketones (Eq. 7).



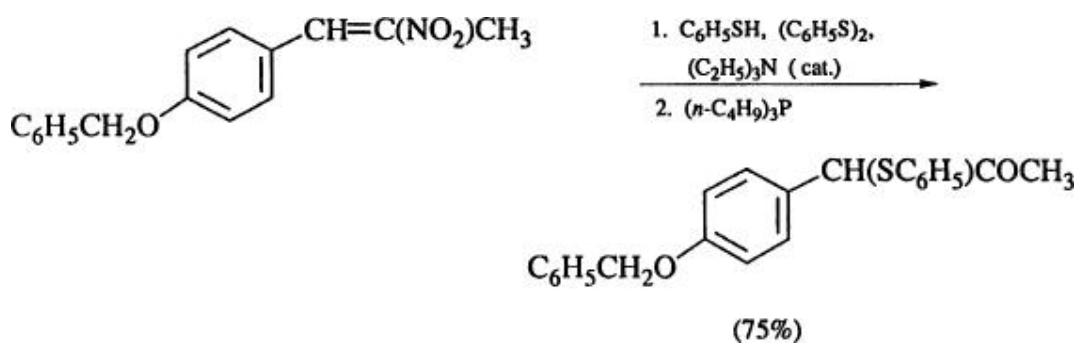
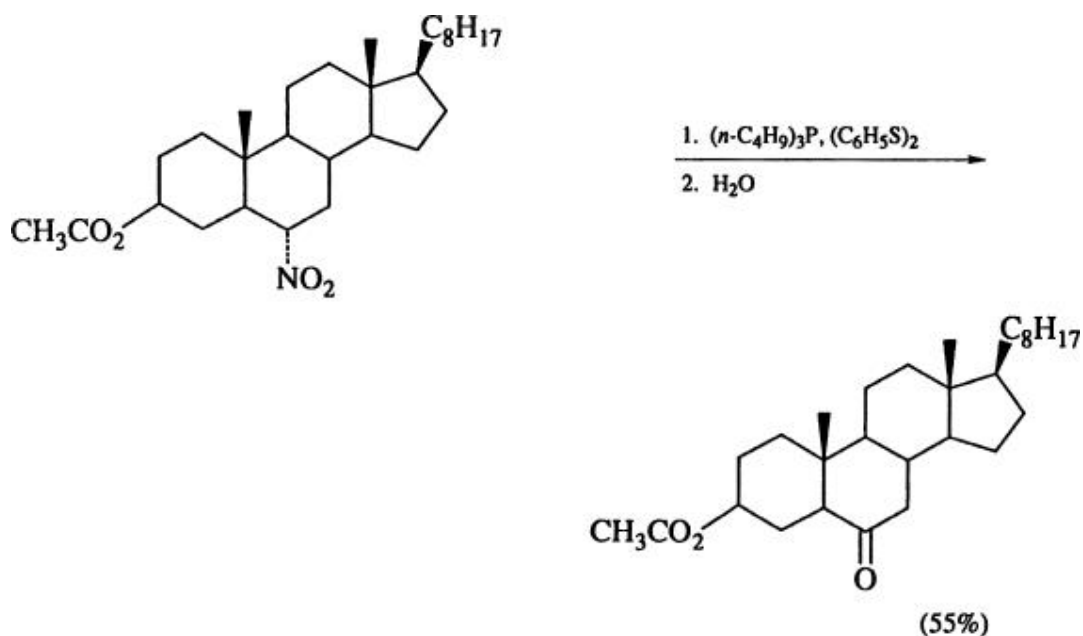
Ammonium persulfate can also be used, but the product yields are lower than with ascorbic acid. (152) Additionally, the use of copper with the ascorbic acid gives saturated 1,4-diketones in 33–46% yields. (152) Zinc chloride catalyzes this conversion, but the yields are lower than with copper and ascorbic acid. (152)

3.3.1.3.5. Tributylphosphine/Diphenyl Disulfide

This reagent provides another very mild method for accomplishing a reductive Nef reaction. Secondary nitro compounds and nitroalkenes give imines, which are hydrolyzed to ketones



upon aqueous workup. A primary nitro compound subjected to these conditions gives a nitrile. (175)

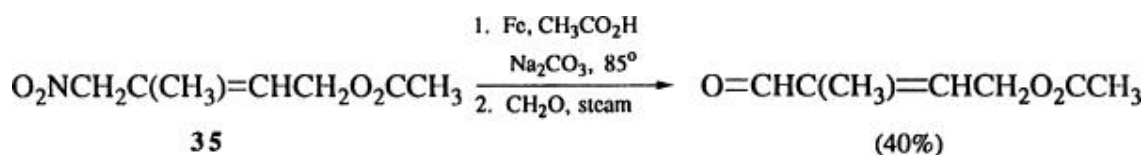


3.3.1.3.6. Formation and Hydrolysis of Oximes

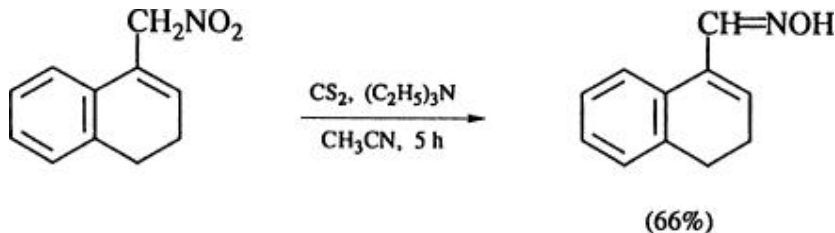
Some reagents transform nitro compounds into oximes that can be hydrolyzed subsequently to give aldehydes or ketones. (176-178) The oldest of these is zinc chloride, usually in the presence of hydrochloric acid (Lucas Reagent).

(179-183) For example, glutaraldehyde dioxime is obtained from 1,5-dinitropentane in 55–60% yield. (180) The only examples of this reaction are with compounds that lack other functionalities which might be hydrolyzed by zinc chloride and hydrochloric acid.

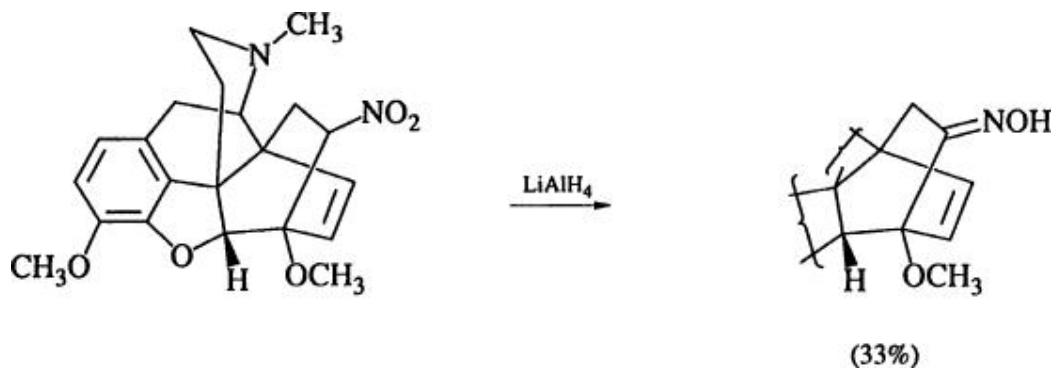
A variety of other reagents can be used to generate oximes from nitro compounds. Copper salts such as copper(II) acetylacetonate catalyze the conversion of nitroparaffins into oximes in 52–89% yields in a carbon monoxide atmosphere and in the presence of diamines. (184) Iron and acetic acid convert nitro compound **35** into the corresponding oxime, which is converted without isolation into the aldehyde by steam distillation in the presence of formaldehyde at pH 2.5 in 40% overall isolated yield. (185) Carbon disulfide and triethylamine



yield oximes from nitro compounds in 29–85% yields under mild conditions. (185a) The most reactive substrates are allyl derivatives.



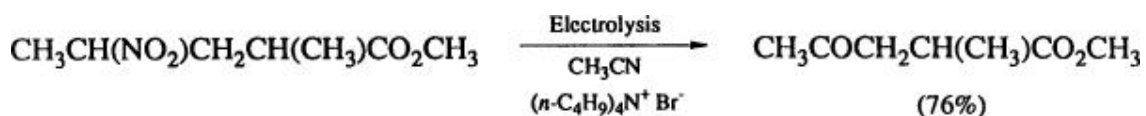
Primary nitro groups give nitriles upon *prolonged* reaction times, as in the case of tributylphosphine and diphenyl disulfide reactions. (175) In an atypical reaction, lithium aluminum hydride converts a nitro amine into the corresponding oxime. (186)



Hydroxylamine *N,N*-disulfonic acid and sulfuric acid convert the salt of nitrocyclohexane into the oxime in 85–90% yield. (187) Basic sodium amalgam or zinc dust also transforms nitro compounds into oximes, (188) as does sulfuric acid with either sodium thiosulfate (189) or hydrogen sulfide. (190) Thus the salt of nitrocyclohexane gives the oxime in 77–80% yields. (189, 190) Finally, β , β -diarylnitro compounds are converted into the corresponding nitronic acids, which give oximes when boiled in methanol. (191)

3.3.1.3.7. Electrolysis

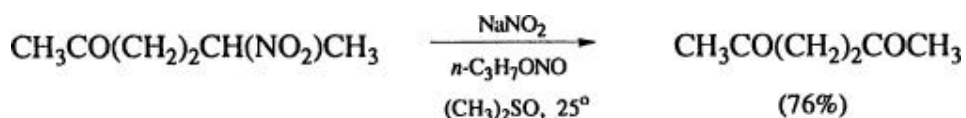
The nitro functionality is a strongly electron-withdrawing group and thus acts as a good electron sink. Consequently, it is not surprising that electrochemical reactions of nitro compounds are possible. Electrolysis of 2-nitropropane gives acetone in 50% yield in addition to a “high boiling residue” which apparently contains 2,3-dimethyl-2,3-dinitrobutane. (192) Nitromethane and nitroethane give *N*-methylhydroxylamine and *N*-ethylhydroxylamine, respectively, when electrolyzed in the presence of trimethylamine. (192) Electrolysis of nitro ketones, nitro esters, and a nitro nitrile in the presence of sodium formate gives 40–90% isolated yields of diketones, keto esters, and a ketonitrile, respectively. (193) Furthermore, electrolysis of nitro compounds in the presence of oxygen produces ketones in 55–86% isolated yields. (194) Both ester and ketone carbonyls as well as ketal groups survive the process. (193-195) Presumably, oxygen is converted into superoxide, which functions as a base in leading to the Nef-like reaction. (194)



3.3.2. Other Reagents

3.3.2.1.1. Sodium Nitrite/Alkyl Nitrites

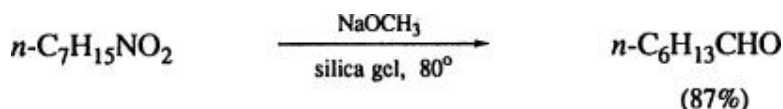
The reagent combination of sodium nitrite and an alkyl nitrite ester in dimethyl sulfoxide is useful because it avoids strong acids or bases. (196-198) The nitro compound is apparently deprotonated by sodium nitrite, and the nitronate anion is nitrosated by the alkyl nitrite. The isolated yields from this room-temperature reaction are 67–90%. (197, 198) Ketones, amides, 1,3-dithianes, and aromatic rings survive the reaction. (197, 198) Carboxylic acids are obtained from primary nitro compounds, while ketones are isolated as expected from secondary nitro systems. (196-198)



3.3.2.1.2. Silica Gel

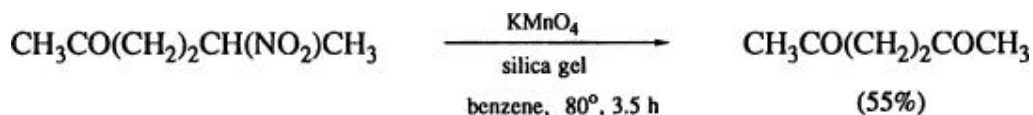
Silica gel can be used to effect the Nef reaction. (152, 199) A solution of a nitronate salt is generated and poured through a column of dry silica gel. The reaction probably occurs because of the acidity of the silica gel and is a true Nef reaction. The yields for the two steps in systems such as those in Eq. 7 (p. 677) with a silica gel second step are 21–73% (diketones) (152) and 26–59% (γ -ketoesters). (199)

Basic silica gel can also be used to obtain Nef products. (200, 201) Silica gel is mixed with methanolic sodium methoxide, the methanol is removed, and the resulting solid is activated at 400° to give a stable, basic silica gel. Nitro compounds are mixed with a large excess of this reagent (typically, a five-fold excess of sodium methoxide is used) (200) and then eluted to give the pure aldehyde or ketone in excellent yields (60–99%). (200) The reaction times are fairly long (48–120 hours); (200, 201) these times can be reduced by using heat, although this can result in lower yields. (201) Despite the basicity of the reagent, aldehydes such as heptanal are obtained in good yields. (200) Ketal, alkene, and ketone functionalities survive these reaction conditions.



Potassium permanganate on silica gel can be used to generate ketones from secondary nitro compounds. (202, 203) A wide variety of 1,4-diketones are obtained in 72–91% yields from γ -nitroketones by combination with a

stoichiometric amount of potassium permanganate on silica gel in benzene at reflux temperatures. Some systems react at room temperature without solvent.

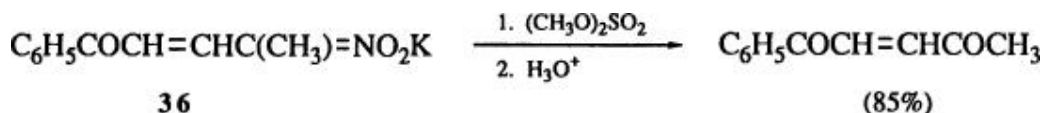


3.4. Related Reactions of Nitro Compounds Leading to Nef Products

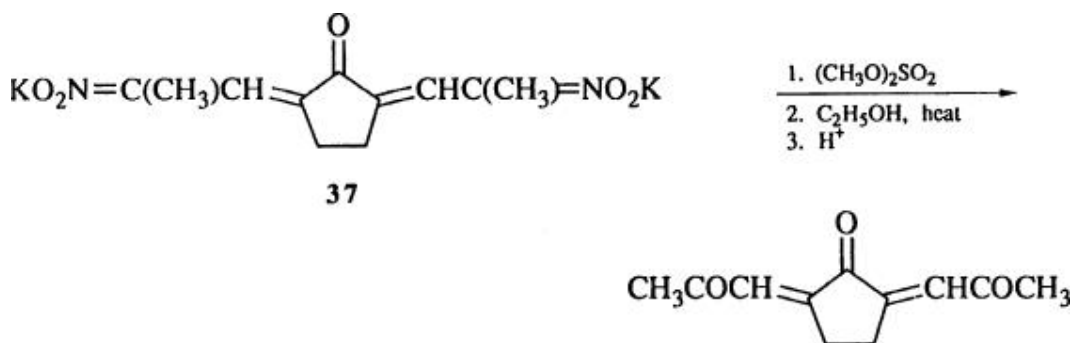
3.4.1.1. Alkylation or Acylation of Nitro Compounds Followed by Hydrolysis

Nitronate anions react with electrophiles on either carbon or oxygen. Protonation leads to either regeneration of the nitro compound or the Nef reaction. Alkylation or acylation normally leads to the O-alkyl (nitronic ester) or O-acyl (nitronic anhydride) products. Nitronic esters are prepared most effectively by alkylation of nitronates with an oxonium salt. (204) They are rapidly converted into carbonyl compounds by aqueous acids. (15) Nitronic anhydrides are generally not stable, (205-208) and those from primary nitro compounds give nitrile oxides which can be trapped by dimethyl acetylenedicarboxylate. (208)

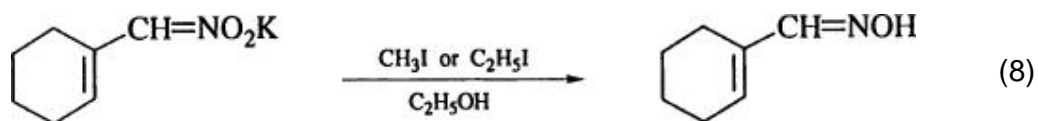
Alkylation of nitro compounds followed by hydrolysis gives carbonyl compounds. (15, 151) For example, nitronate **36** gives an 85% yield of the corresponding



diketone upon treatment with dimethyl sulfate and hydrolysis. (151) Dinitronate **37** gives the corresponding trione in 55% yield. (151) An oxime is obtained



by this procedure in ethanol (Eq. 8), but no reaction occurs in either diethyl ether



or benzene, presumably because of insolubility of the nitronate salt. (209)

Acylation of nitronates gives the *O*-acylnitronic anhydrides as relatively unstable intermediates. (205-208) Some of these products can be isolated, albeit in low yields (Eq. 9). (205) Hydrolysis of the product from Eq. 9 with water gives

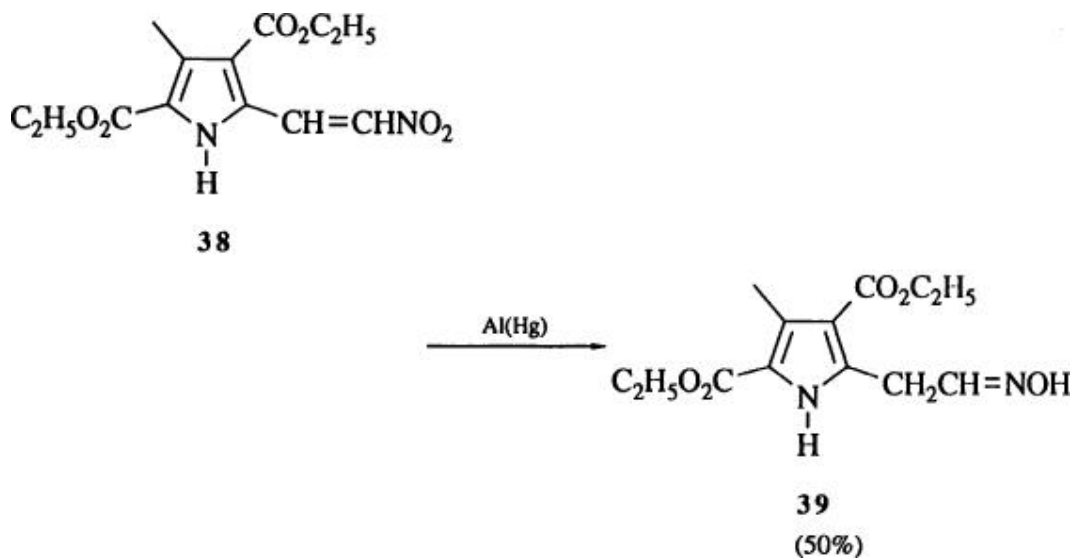


acetone and acetic acid. Primary nitroparaffins are oxidized to carboxylic acids with acetic anhydride and weak bases. (206-208) For example, benzoic acid is obtained in 78% yield by refluxing phenylnitromethane with acetic anhydride and sodium acetate followed by hydrolysis. (208)

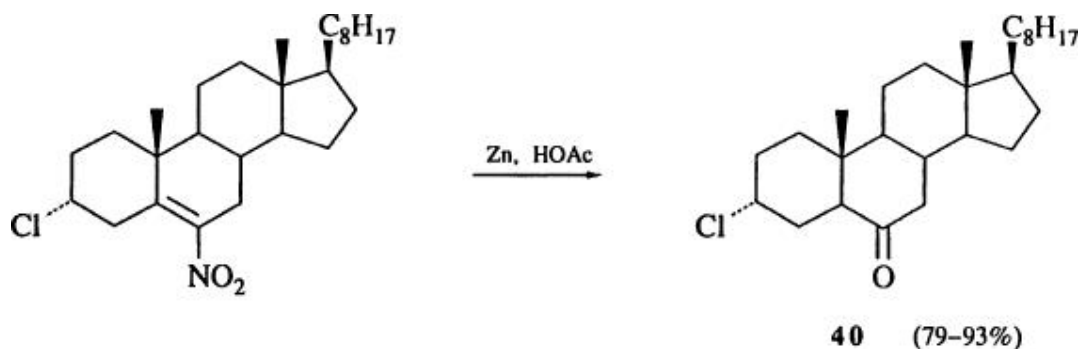
3.4.1.2. Reactions of Nitroolefins

Conjugated nitroolefins are used as acceptors for many nucleophiles to provide useful substrates for the Nef reaction, as seen in earlier sections of this chapter; however, there are other reactions where the nitroolefin is converted directly into a Nef product.

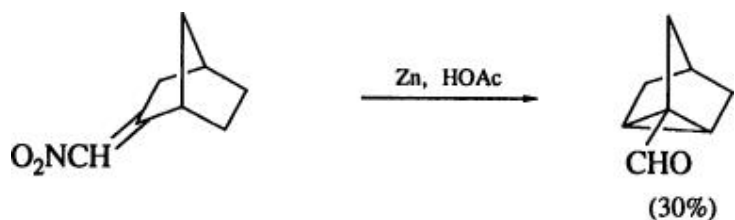
Nitroolefins can be reduced by metals to give either oximes or ketones. For example, aluminum amalgam converts the polyfunctional molecule **38** into the oxime **39**. (210) More recent work utilizes zinc in acetic acid for this



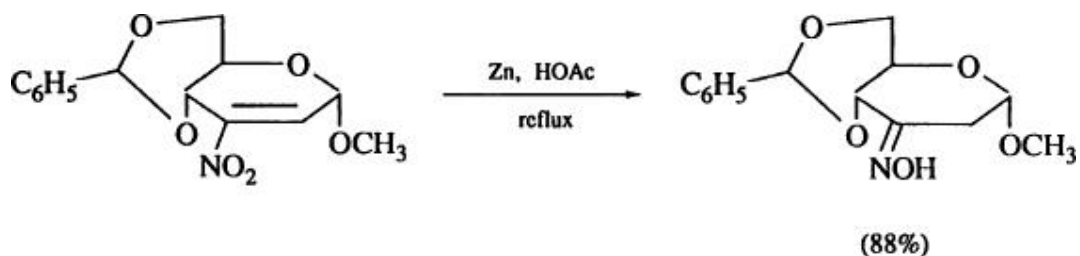
conversion. (211-214) For example, 6-nitrocholesteryl chloride gives the ketosteroid **40** in 79–93% yields when allowed to react under these conditions. (211, 212)



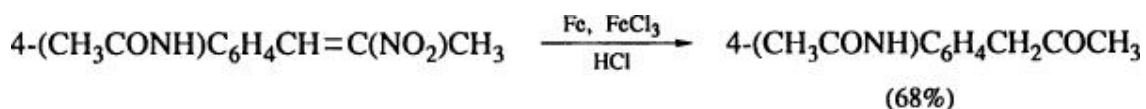
Rearrangements can occur, (214) however, several methylpyranosides containing



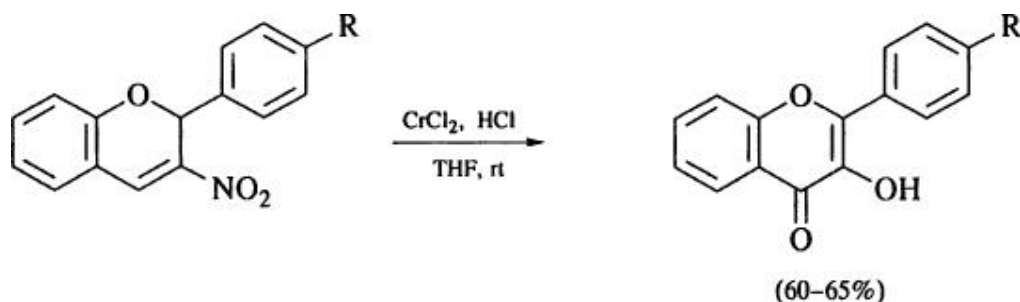
nitroolefin groups produce the corresponding oximes in high yields, (213) showing that acetal groups survive such treatment. Iron and iron(III) chloride react



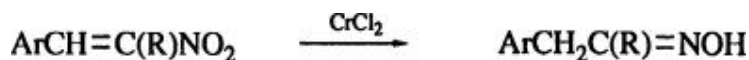
with nitrostyrenes in hydrochloric acid to give ketones in a wide variety of systems. [213a](#)



Chromium(II) chloride also produces ketones in 52–81% yields from nitroolefins. [\(215\)](#) This is in contrast to earlier reports of their conversion into α -hydroxyketones, [\(216-218\)](#) which were initially proposed to arise by reduction to the nitroso alkene. Chromium(II) chloride can be used to obtain α -diketones



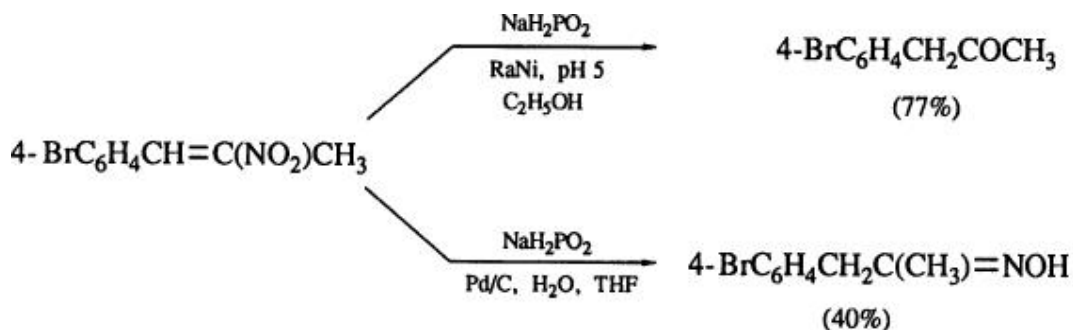
via the same types of intermediates. [\(219\)](#) Some acyclic β -aryl- α , β -unsaturated nitroolefins give saturated oximes with chromium(II) chloride. [\(220\)](#)



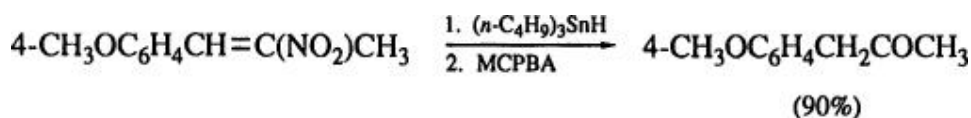
Stannous chloride in alcohols or thiols converts nitro compounds into the corresponding α -alkoxy or α -alkylthio ketones. [\(221\)](#) For example, this reagent converts nitrocyclohexene in ethanol into 2-ethoxycyclohexanone in

79% yield.

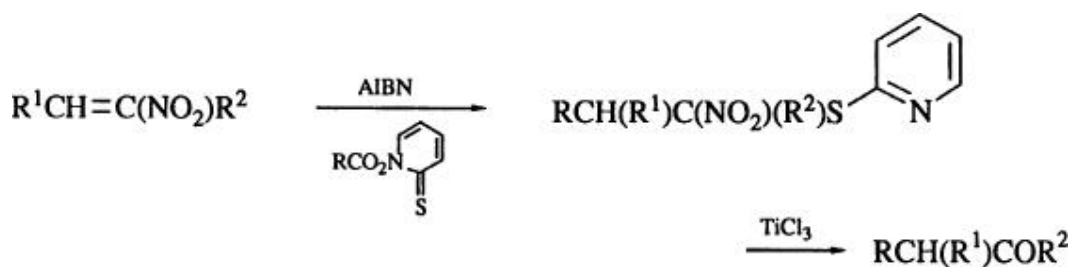
Other reducing agents give various results. Sodium borohydride (213) or *o*-phenylenediamine aminals (222) give saturated nitro compounds. Sodium borohydride/3 gives hydroxylamines by reduction of the intermediate nitronates. (223) Lithium tri-*sec*-butylborohydride converts nitroalkenes into ketones after acid hydrolysis in 80–83% yields. (224) The inverse addition of lithium aluminum hydride to terminal nitroalkenes gives aldimines. (225) A combination of sodium hypophosphite and Raney nickel reduces nitroolefins to ketones in 52–92% yields without affecting other functional groups such as esters and aromatic nitro groups. (226) Sodium hypophosphite and palladium convert nitroolefins into oximes. (227) Some nitroolefins are converted into α -chloro oximes



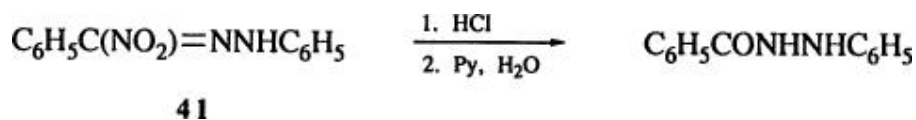
in good yield by exposure to gaseous hydrogen chloride in ether. (228) Tributyltin hydride reduces nitroalkenes to tributyltin nitronate esters, which react with *m*-chloroperoxybenzoic acid or ozone to give aldehydes or ketones. (228a)



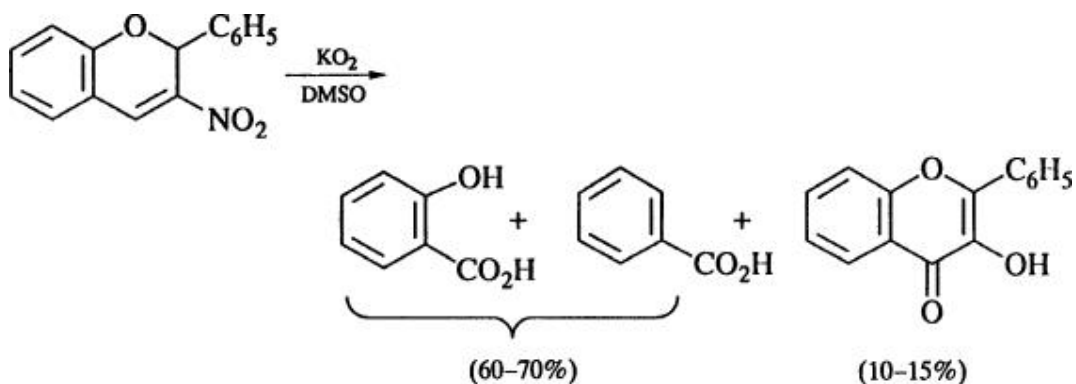
Free-radical addition of nitroolefins to substituted thiopyridones in the presence of azobis(isobutyronitrile) (AIBN) gives adducts which are decomposed with titanium trichloride to yield ketones or acids in good yields. (229)



Nitrohydrazones such as **41** give acylhydrazines after treatment with hydrochloric acid followed by aqueous pyridine. (230, 231)

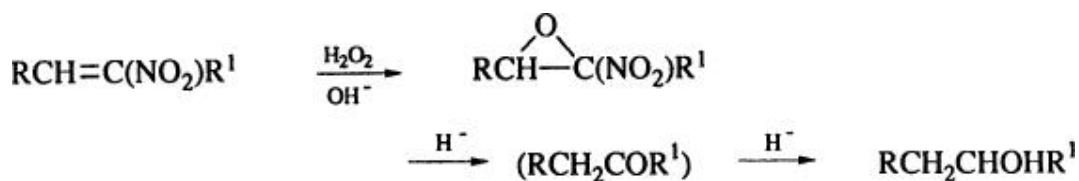


Potassium superoxide produces flavanols in low yields from nitroalkenes. The major products are salicylic acids and benzoic acids. (231a)



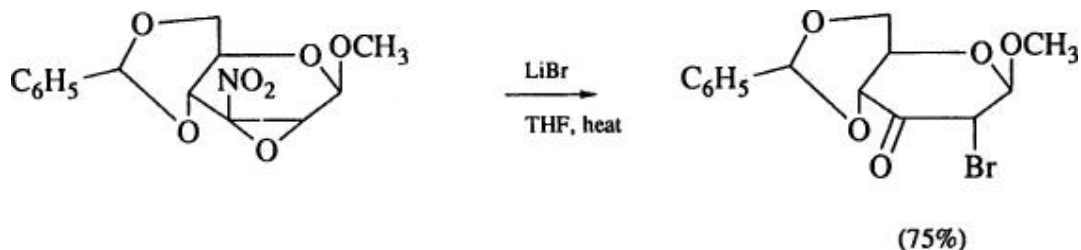
3.4.1.3. Reactions of Nitroepoxides

Conjugated nitroolefins can be converted into the corresponding nitroepoxides with basic hydrogen peroxide. (232) Reduction with lithium aluminum hydride (232) or sodium borohydride (233) gives the

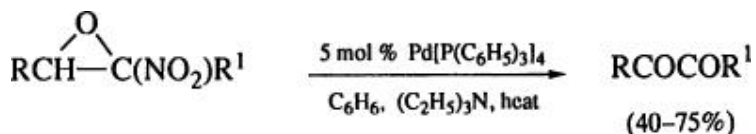


alcohol expected from reduction of the Nef product. Opening of the epoxide with nucleophiles other than hydride yields α -substituted ketones. (234-235b)

Catalytic

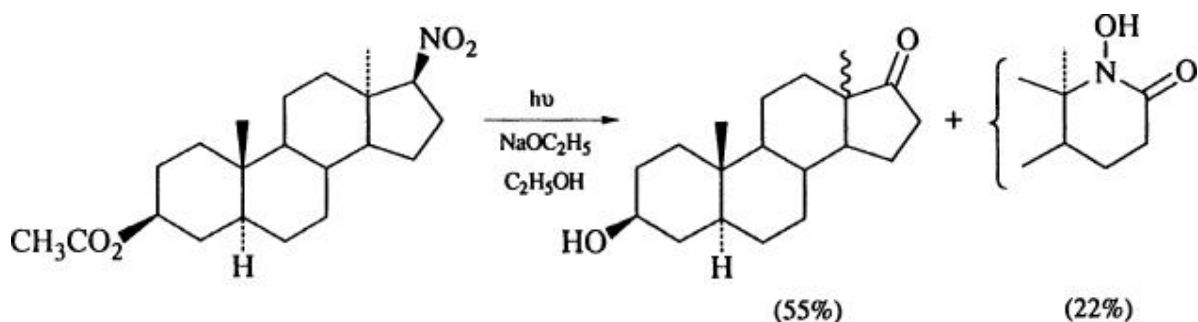


palladium tetrakis(triphenylphosphine) converts several nitroepoxides into 1,2-diketones. (236)

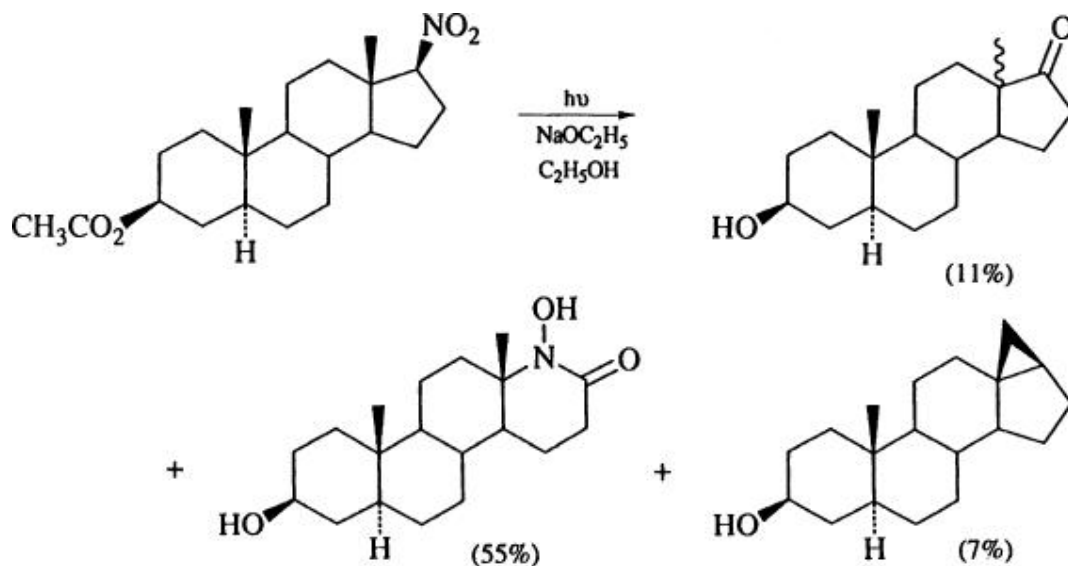


3.4.1.4. Photolysis

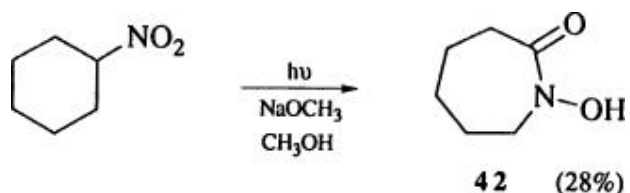
There are a few reports of the photolysis of nitro compounds where Nef products are formed. Several nitrosteroids undergo photolysis (237-239) in the presence of a base such as sodium ethoxide in ethanol to give ketones and hydroxamic acids as major products. (239) No ketone is obtained



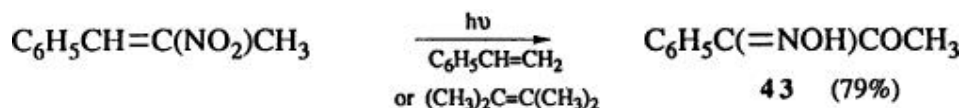
from photolysis in isopropyl alcohol or diethyl ether. (237) The corresponding nitro compound with a 13β methyl group gives 11% of the ketone, 55% of the hydroxamic acid, and 7% of a cyclopropane. (239) It is surprising that irradiation



of this nitrosteroid with sodium methoxide in methanol gives 78% of the hydroxamic acid and only 1% of the ketone. (238) It is not clear if the choice of alkoxide base is critical, but this seems to be the only explanation consistent with the reported facts. In many nonsteroidal systems, the predominant reaction product is also the hydroxamic acid, as with nitrocyclohexane and sodium methoxide, which gives the *N*-hydroxylactam **42** in 28% yield. (238)



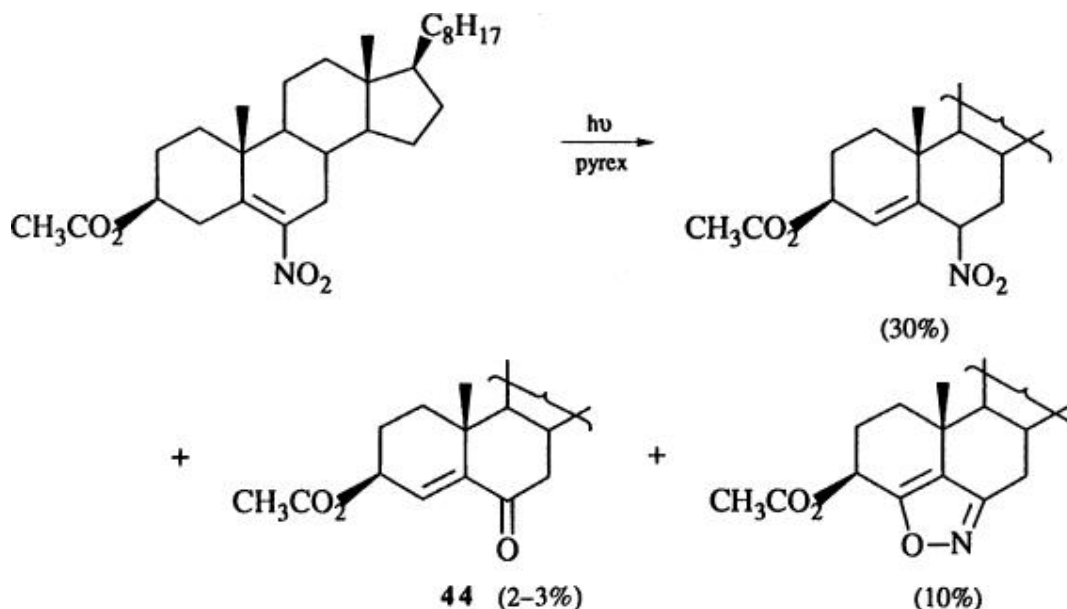
Several reports deal with the photochemistry of unsaturated nitro compounds. (240-243) For example, irradiation of β -methyl- β -nitrostyrene in the presence of either styrene or 2,3-dimethyl-2-butene gives the keto oxime **43** in 79% yield. (240) In acetone, **43** is obtained in 80% yield, but benzaldehyde (6%)



is also detected. (242) With the analogous *p*-nitro compound, a 61% yield of the keto oxime is formed along with *p*-nitrobenzaldehyde (15%). (242) Photolysis of 9-nitroanthracene gives anthraquinone in 21% yield in addition to

10,10 -bianthrone (55%). The use of nitric oxide during this latter reaction increases the yield of anthraquinone to 77% while that of bianthrone drops to 9%. (240) β -Nitrostyrene is reduced by photolysis in the presence of *N,N* -dioctyl-4,4 -bipyridinium dibromide and ruthenium tris(bipyridine) dichloride to give phenylacetaldehyde and/or the corresponding oxime. (243)

The photolysis of nitroolefins without any added base or participating solvent has also been reported. 6-Nitrocholesteryl acetate gives the $\Delta^{4,5}$ isomer in 30% yield in addition to 2–3% of the corresponding enone 44 and 10%



of an oxazole. (241) γ -Hydrogen abstraction occurs to give the conjugated nitronic acids as intermediates in the formation of enones. (244) Several nitronic acids yield ketones upon irradiation, but other products are also formed. (244)

3.5. Synthetic Utility

The common occurrence of the carbonyl group in organic molecules makes the Nef reaction significant in organic synthesis. The nitro functionality is most commonly introduced as a nucleophile—either a nitronate anion or nitrite ion. The Nef reaction allows the nitronate anion to become an acyl anion equivalent of great utility—particularly from conjugate addition reactions.

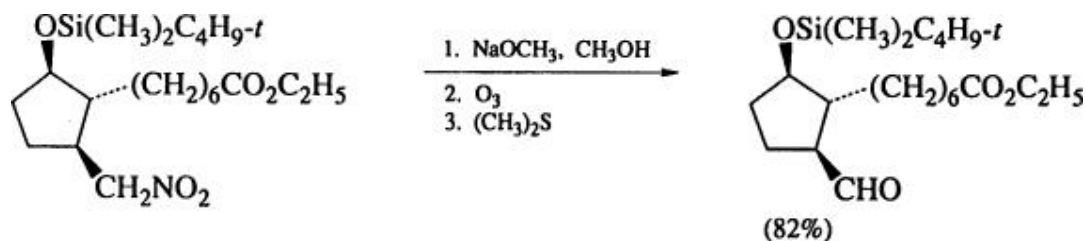
Even though many aldehydes and ketones, including many that are sensitive like those containing a β -lactam (2), can be prepared by the Nef reaction, this process suffers from several problems. Traditionally, the reaction is carried out in an aqueous medium so that higher molecular weight nitro compounds do not perform well. The use of water-miscible organic cosolvents largely

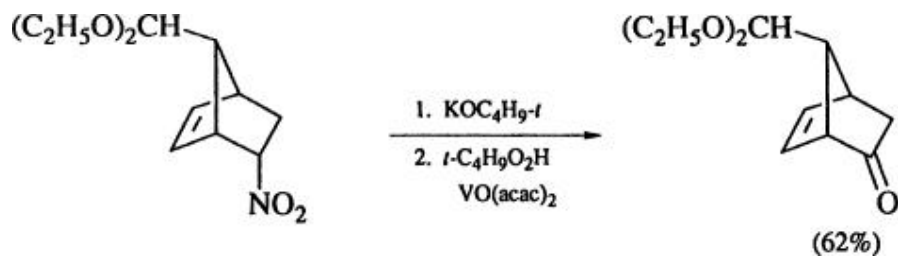
overcomes this deficiency. A more serious problem is the harshness of the reaction conditions, especially the pH of the Nef process. Numerous polyfunctional molecules undergo side reactions as a result. Modified Nef reactions avoid this difficulty by the use of milder conditions, as shown in Eq. 4. The most significant of these approaches involve potassium permanganate, ozone, or titanium trichloride.

It is not easy to generalize on which methods will work best with a new nitro compound since efficiency seems to be highly dependent upon the substrate. That is, one method will work better with some nitro compounds while another method will be superior with other compounds. Nevertheless, some information may be gleaned from methods used on related substrates in Table I.

It is clear that nitro compounds of lower molecular weight can be converted into the carbonyl product in many ways. The absence of other functional groups widens the choice of methods that can be used, although the traditional Nef reaction may be among the best. For example, nitrocyclohexane gives cyclohexanone in 85–97% yields when treated with base followed by acid. (10, 16) Potassium permanganate with aqueous hydroxide effects this transformation in quantitative yield, (16) but the yield drops to 93% when methanol is the solvent. (131) Some other modified Nef approaches are only slightly less effective; for example, cyclohexanone is obtained in very good yields when nitrocyclohexane is allowed to react with *tert*-butyl hydroperoxide-oxovanadium(IV) bisacetylacetonate (86%), (144) molybdenum peroxide (86%), (145) or ceric ammonium nitrate (80%). (148) Sodium methoxide on silica gel effects a 99% conversion. (200)

As the complexity of the substrate increases, the choice of viable methods is reduced sharply. Ester or acetal groups rarely survive either the usual Nef reaction conditions or nonbuffered titanium trichloride. (154, 156) Such acid-sensitive compounds are best treated with permanganate, buffered titanium trichloride,





or ozone. The last method cannot be used with unsaturated systems or acetals unless the amount of ozone is carefully controlled. Several specific reactions are shown to illustrate selectivity (see also compound [2](#)).

4. Experimental Procedures

4.1.1.1. 3-endo-Methylbicyclo[2.2.1]heptan-2-one (Sodium Hydroxide and Sulfuric Acid) (8)

3-exo-Methyl-2-endo-nitrobicyclo[2.2.1]heptane (35.6 g, 0.23 mol) was added to a solution of sodium hydroxide (12 g, 0.3 mol) in 150 mL of water. After 2 hours, deprotonation was complete and the reaction mixture was filtered and extracted with ether to remove any neutral organic compounds. The nitronate solution was added slowly dropwise to a well-stirred solution of 25 mL of concentrated sulfuric acid in 150 mL of water at 0–5°. Nitrous oxide was evolved and the reaction mixture turned blue-green. Extraction with three 50-mL portions of ether gave, after distillation, 3-endo-methylbicyclo[2.2.1]heptan-2-one: 14.5 g (51%), bp 59–61.5° (10 mm), n_D^{25} 1.4677, 2,4-dinitrophenylhydrazone mp 114–118°, semicarbazone mp 185–187°.

4.1.1.2. Methyl 4-Oxo-2-phenylpentanoate (Hydrochloric Acid) (37)

Methyl phenylacetate (0.075 g, 0.5 mmol) was added dropwise to 0.6 mmol of lithium diisopropylamide dissolved in 3 mL of tetrahydrofuran at –78° under nitrogen. After 30 minutes of stirring, the reaction mixture was cooled to –100° (dry ice/ether), and 0.065 g (0.75 mmol) of 2-nitropropene was added dropwise. Stirring was continued while the temperature was allowed to rise slowly to 10° over 5 hours. Dilute hydrochloric acid (3 mL of 17% acid) was added at 0°, and the mixture was stirred overnight at 0°. Dilution with water and extraction with methylene chloride gave a crude product which was purified by preparative TLC to give 0.081 g (79%) of methyl 4-oxo-2-phenylpentanoate: mp 70–71°; IR (NaCl) 1740–1710 cm⁻¹; ¹H NMR (CDCl₃) δ 2.12 (s, 3H), 2.67 (dd, *J* = 4 and 18 Hz), 3.36 (dd, *J* = 10 and 18 Hz, 1H), 3.60 (s, 3H), 4.07 (dd, *J* = 4 and 10 Hz, 1H), 7.22 (s, 5H).

4.1.1.3. 2-(1-Cyanocyclohexyl)-2-methylpropanal (Sodium tert-Butoxide and Potassium Permanganate) (127)

A 60% oil dispersion of sodium hydride (0.20 g, 5.0 mmol) was washed with pentane under nitrogen and was mixed with 20 mL of *tert*-butyl alcohol. The mixture was stirred for 10 minutes while a solution of 2-(1-cyanocyclohexyl)-2-methyl-1-nitropropane (0.42 g, 2.0 mmol) in 20 mL of *tert*-butyl alcohol was added. After 20 minutes of additional stirring, 400 mL of ice-cold pentane was added followed by 50 g of ice and an ice-cold solution of potassium permanganate (0.237 g, 1.5 mmol) in 80 mL of water. The reaction mixture was stirred for 10 minutes, and 2 mL of 1 M sodium metabisulfite was added followed by 4 mL of 1 M sulfuric acid. The phases were separated and the aqueous layer was extracted with pentane. The combined organic layers were washed with brine to give, after drying, concentration, and flash

chromatography on silica gel using benzene–pentane (1:1), 0.293 g (82%) of 2-(1-cyanocyclohexyl)-2-methylpropanal: mp 61.5–62°; $^1\text{H NMR}$ (CDCl_3) δ 1.22 (s, 6H), 1.3–2.2 (m, 10H), 9.72 (s, 1H); IR (KBr) 2720, 2220, 1710 cm^{-1} .

4.1.1.4. Dimethyl 4-Oxopimelate (Sodium Methoxide and Ozone) (141)

Dimethyl 4-nitropimelate (4.66 g, 0.02 mol) was dissolved in 50 mL of anhydrous methanol and stirred with sodium methoxide (1.08 g, 20 mmol) for 10 minutes. This solution was cooled to -78° , and ozone/oxygen was bubbled through until an excess had been used as evidenced by a light-blue color. The ozone generator was turned off, and after 30 minutes nitrogen was bubbled through to remove excess ozone, and 5 mL of dimethyl sulfide was added. The reaction mixture was allowed to warm to room temperature and stand for 16 hours. It was concentrated and the residue was dissolved in ether and washed with water. Evaporation of the solvent gave the crude product, which was recrystallized from hexane to give 3.55 g (88%) of dimethyl 4-oxopimelate, mp 49–50°.

4.1.1.5. Cyclohexanone [Oxovanadium(IV) Bisacetylacetonate] (144)

Nitrocyclohexane (0.129 g, 1.00 mmol) was stirred at room temperature with 0.123 g (1.10 mmol) of potassium *tert*-butoxide in 2 mL of benzene for 15 minutes. A solution of 0.3 mL of 90% *tert*-butyl hydroperoxide, 3.5 mg of oxovanadium(IV) bisacetylacetonate, and 0.7 mL of benzene was added over a 15-minute period. After 20 minutes, the mixture was diluted with ether, washed with water and brine, and dried and the solvent was evaporated to give the equivalent of 0.84 g (89%) of cyclohexanone determined by GC.

4.1.1.6. Cyclohexanone [Oxidiperoxomolybdenum(VI), Pyridine, HMPA] (145)

Nitrocyclohexane (0.43 g, 3.3 mmol) in 20 mL of tetrahydrofuran was added dropwise over a 5-minute period to a solution of diisopropylamine (0.90 mL, 6.7 mmol) and 2.8 mL (6.7 mmol) of *n*-butyllithium in hexane in 20 mL of tetrahydrofuran at -78° . The molybdenum peroxide pyridine HMPA complex (2.86 g, 6.6 mmol) was added quickly to the nitronate anion and the reaction mixture was allowed to warm to room temperature over 3 hours. The mixture was quenched with 40 mL of saturated aqueous sodium sulfite and was extracted twice with ether. The organic layers were washed with 5% hydrochloric acid, dried, and the solvent was evaporated to give 0.28 g (86%) of pure cyclohexanone after distillation.

4.1.1.7. Cyclohexanone (Ceric Ammonium Nitrate) (148)

Nitrocyclohexane (0.65 g, 5.0 mmol) was stirred rapidly with 5 mL of triethylamine, and 14 mL of acetonitrile and ceric ammonium nitrate (2.75 g, 5.0 mmol) in 6 mL of water was added. The deep brown emulsion which formed was heated to 50° for 2 hours, cooled, diluted with acetonitrile, and filtered. The filtrate was dissolved in 100 mL of ether and washed with water

and dilute hydrochloric acid. Evaporation of the solvent gave 0.40 g (81%) of cyclohexanone.

4.1.1.8. 6-Methylcyclohex-3-en-1-one (Titanium Trichloride and Ammonium Acetate) (154)

An excess of buffered titanium trichloride was formed by mixing 4.6 g (0.06 mol) of ammonium acetate in 15 mL of water with 0.01 mol of 20% aqueous titanium trichloride. 5-Methyl-4-nitrocyclohexene in tetrahydrofuran was added rapidly and the reaction mixture was stirred for 45 minutes at room temperature. The reaction mixture was extracted with ether, the organic layers were washed with 5% sodium bicarbonate and brine and dried. Evaporation of the solvent gave 6-methylcyclohex-3-en-1-one in 60% yield: IR 3040, 1715 cm^{-1} ; 2,4-dinitrohydrazone, mp 141°.

4.1.1.9. 3-(1-Methyl-2-oxocyclohexyl)-2-butanone (Titanium Tetrachloride) (167)

2-Nitro-2-butene (0.15 g, 1.5 mmol) was added rapidly to a solution of titanium tetrachloride (1.0 mmol) in 4 mL of methylene chloride under nitrogen at -78° . After 10 minutes of stirring, 2-methyl-1-trimethylsilyloxycyclohexene (0.18 g, 1.0 mmol) was added dropwise over 5 minutes. After another hour, the temperature was allowed to rise to 0° over 2 hours, and 1.5 mL of water was added. The reaction mixture was heated to reflux for 2 hours, cooled, and extracted with ethyl acetate. Evaporation of the solvent gave a residue which was filtered through alumina and distilled to give 0.13 g (71%) of 3-(1-methyl-2-oxocyclohexyl)-2-butanone: bp 88–89° (0.2 mm); IR (NaCl) 1701 cm^{-1} ; $^1\text{H NMR}$ (CCl_4) δ 1.03 (s, 3H), 1.01 (d) and 1.15 (d, $J = 7.5$ Hz, 3H), 2.07 (s) and 2.10 (s) (3H), 2.80 (q) and 2.93 (q, $J = 7.5$ Hz, 1H).

4.1.1.10. Cyclohexanone (Sodium Methoxide and Silica Gel) (200)

Nitrocyclohexane (0.5 g, 3.9 mmol) was mixed with 50 g of basic silica gel (prepared by mixing methanolic sodium methoxide with silica gel, evaporating the solvent to dryness, and activation at 400° for several hours—the amount of sodium methoxide per kilogram of silica gel was 0.5 molar equivalent). After 48 hours at room temperature, elution of the yellow silica gel with ether and evaporation of the solvent gave 0.38 g (99%) of cyclohexanone, pure by chromatography.

4.1.1.11. Undecane-2,5-dione (Potassium Permanganate and Silica Gel) (203)

A solution of 5-nitroundecan-2-one (0.97 g, 4.5 mmol) in 30 mL of benzene was added to 15 g of potassium permanganate on silica gel [prepared from 1.18 g (7.5 mmol) of aqueous potassium permanganate and 15 g of silica gel after drying at 100° in a vacuum], and the mixture was stirred at reflux for 10 hours. The mixture was filtered and the solid was washed several times with ether. Evaporation of the solvent gave crude product which was passed through a column of alumina to give 0.33 g (40%) of undecane-2,5-dione,

which was about 90% pure by ^1H NMR.

5. Tabular Survey

An attempt has been made to include all known examples of the Nef reaction published through late 1988 in Table I. Entries in the table are organized by increasing number of carbon atoms in the basic structure of the nitro or nitronate substrate, excluding carbon atoms in ester and ether groups that are not involved in the reaction. Multiple products are given with the Nef product first. A dash in the yield column indicates that a yield was not reported. Some products are isolated as derivatives and are indicated with a D (2,4-dinitrophenylhydrazone), P (phenylhydrazone), A (anilide), or B (benzylphenylhydrazone). Unsuccessful Nef reactions are not given (see section on Side Reactions).

Abbreviations used in the table are as follows:

A	anilide
Ac	acetyl
acac	acetylacetonate
AIBN	azobis(isobutyronitrile)
8-Azaflavin	structure 28
B	benzylphenylhydrazone
CAN	ceric ammonium nitrate
D	2,4-dinitrophenylhydrazone
DBU	1,8-diazabicyclo[4.4.0]undec-7-ene
DMF	dimethylformamide
DMS	dimethyl sulfide
DMSO	dimethyl sulfoxide
e ⁻	electrolysis
HMPA	hexamethylphosphoric triamide
LDA	lithium diisopropylamide
LICA	lithium isopropylcyclohexylamide
MCPBA	<i>m</i> -chloroperoxybenzoic acid
MIBA	<i>m</i> -iodobenzoic acid
P	phenylhydrazone
Py	pyridine
RaNi	Raney nickel
rt	room temperature
TBDMS	<i>tert</i> -butyldimethylsilyl
TMBG	<i>N,N,N',N'</i> -tetramethyl- <i>N</i> ² - <i>tert</i> -butylguanidine

TMS trimethylsilyl
Ts *p*-toluenesulfonyl

Table I. Nef Reaction of Nitro Compounds

[View PDF](#)

TABLE I. NEF REACTION OF NITRO COMPOUNDS

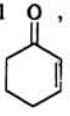
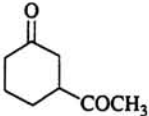

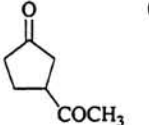
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
C ₁ CH ₃ NO ₂	1. OH ⁻ 2. H ⁺	CH ₂ O (—)	16
	1. CH ₂ =CHCOCH ₃ , Al ₂ O ₃ 2. H ₂ O ₂ , K ₂ CO ₃	CH ₃ CO(CH ₂) ₂ CO(CH ₂) ₂ COCH ₃ (48)	245
	1. CH ₂ =CHCOC ₂ H ₅ , Al ₂ O ₃ 2. H ₂ O ₂ , K ₂ CO ₃	C ₂ H ₅ CO(CH ₂) ₂ CO(CH ₂) ₂ COC ₂ H ₅ (50)	245
C ₂ CH ₃ CD ₂ NO ₂ C ₂ H ₅ NO ₂	1. NaOH 2. H ₂ SO ₄	CH ₃ CDO (70)	246
	1. OH ⁻ 2. HCl	CH ₃ CHO (70)	2
	1. OH ⁻ 2. H ⁺	" (77)	16
	1. Ca(OH) ₂ 2. H ₂ SO ₄	" (77)	21
	NaOH, 8-azaffavin (28)	" (—)	139
	1. CrCl ₂ , CH ₃ OH 2. HCl	" (32-D)	172
	1.  , Al ₂ O ₃	 (68)	245
	2. H ₂ O ₂ , K ₂ CO ₃		
	1.  , Al ₂ O ₃	 (80)	245
	2. H ₂ O ₂ , K ₂ CO ₃		

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)



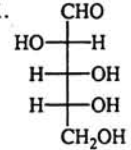
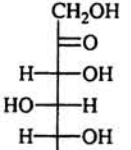
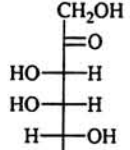

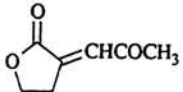

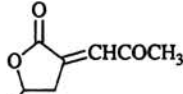

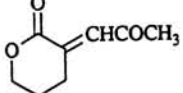
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$, $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$, CH_3CN , e^-	$\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{CH}_3$ (60)	194
	$\text{CH}_3\text{CH}=\text{CHCO}_2\text{CH}_3$, $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$, CH_3CN , e^-	$\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{CH}_3$ (59)	194
	O , $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$, CH_3CN , e^- 	 (57)	194
	$\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$, $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$, CH_3CN , e^-	$\text{CH}_3\text{COCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ (46)	194
$\text{HOCH}_2\text{CH}=\text{NO}_2\text{Na}$	1. CHO  2. H_2SO_4	 (23) + 	247, 248
C_3 $(\text{CH}_3)_2\text{NCH}=\text{C}(\text{NO}_2)\text{CH}_3$	1. LICA 2. $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_5-t$ 3. Silica gel	$\text{CH}_3\text{COCH}=\text{CHCO}_2\text{C}_6\text{H}_5-t$ (7)	199
	1. LICA 2. $\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ 3. Silica gel	$\text{CH}_3\text{COCH}=\text{C}(\text{C}_6\text{H}_5)\text{CO}_2\text{C}_2\text{H}_5$ (28)	199
	1. LICA 2. $\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$	" (—)	199
	3. NaHCO_3 , $(\text{CH}_3\text{O})_2\text{SO}_2$ 4. H_3O^+ , heat		
	1. LICA 2. 4- $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CO}_2\text{CH}_3$ 3. Silica gel	$\text{CH}_3\text{COCH}=\text{C}(\text{CO}_2\text{CH}_3)\text{C}_6\text{H}_4\text{OCH}_3-4$ (22)	199
	1. LICA 2. $\text{CH}_3\text{COSC}_2\text{H}_5$ 3. CH_3OH , heat	$\text{CH}_3\text{COCH}=\text{CHCO}_2\text{CH}_3$ (7)	199
	1. LICA 2. $\text{CH}_3\text{COSC}_2\text{H}_5$ 3. Silica gel	$\text{CH}_3\text{COCH}=\text{CHCOSC}_2\text{H}_5$ (14)	199
	1. LICA 2. $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ 3. Silica gel	$\text{CH}_3\text{COCH}=\text{CHCO}_2\text{C}_2\text{H}_5$ (18)	199
	1. LICA 2. $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ 3. NaHCO_3 , $(\text{CH}_3\text{O})_2\text{SO}_2$ 4. H_3O^+ , heat	" (—)	199
	1. LICA 2. 		(—) 199
	3. NaHCO_3 , $(\text{CH}_3\text{O})_2\text{SO}_2$ 4. H_3O^+ , heat		
	1. LICA 2. 		(42) 199
	3. Silica gel 1. LICA 2. 		(24) 199

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
<i>n</i> -C ₃ H ₇ NO ₂	3. Silica gel 1. LICA 2. <i>n</i> -C ₃ H ₇ CO ₂ C ₄ H ₉ - <i>t</i> 3. Silica gel	CH ₃ COCH=C(C ₂ H ₅)CO ₂ C ₄ H ₉ - <i>t</i> (24)	199
	1. NaOH 2. H ₂ SO ₄	C ₂ H ₅ CHO (80)	16, 21
	1. Ca(OH) ₂ 2. H ₂ SO ₄	" (80)	21
	NaOH, 8-azaflavin (28)	" (—)	139
	1. CrCl ₂ , CH ₃ OH 2. HCl	" (66-D)	172
	Silica gel, NaOCH ₃	" (97)	200
	NaNO ₂ , <i>n</i> -C ₃ H ₇ ONO, DMSO	" (70)	197
	NaOH, (NH ₄) ₂ S ₂ O ₈	" (45-59) + C ₂ H ₅ CH(NO ₂)CH(NO ₂)C ₂ H ₅ (41)	150
	1. (C ₂ H ₅) ₃ N 2. MoO ₅ ·Py·HMPA	C ₂ H ₅ CO ₂ H (69)	145
	<i>i</i> -C ₃ H ₇ NO ₂	1. CH ₂ =CHCOCH ₃ , Al ₂ O ₃ 2. H ₂ O ₂ , K ₂ CO ₃	C ₂ H ₅ CO(CH ₂) ₂ COCH ₃ (60)
1. OH ⁻ 2. HCl		(CH ₃) ₂ CO (67)	2
1. NaOH 2. HCl		" (76-D)	10
1. NaOH 2. H ₂ SO ₄		" (73-84)	21
1. Ca(OH) ₂ 2. H ₂ SO ₄		" (84)	21
1. NaOH 2. Ac ₂ O 3. H ₂ O, heat		" (—, D)	205
1. KOH, MgSO ₄ 2. KMnO ₄		" (96-D)	124
1. KOH, CH ₃ OH 2. KMnO ₄ , MgSO ₄		" (85)	131
1. NaOH 2. O ₂		" (83)	138
NaOH, 8-azaflavin (28) NaNO ₂ , <i>n</i> -C ₃ H ₇ ONO, DMSO Silica gel, NaOCH ₃ NaOH, e ⁻		" (—) " (70) " (97) " (50)	139 197 200 192
1. CrCl ₂ , CH ₃ OH 2. HCl	" (77-D)	172	
1. NaOH 2. Ac ₂ O 3. H ₂ O, heat (C ₂ H ₅) ₄ N ⁺ F ⁻ (cat.)	" (—, D) " (90) " (57) + (CH ₃) ₂ C(NO ₂)NO (32)	205 249 74	
NaOH, Na ₂ S ₂ O ₈	" (8-27-D) I + [(CH ₃) ₂ C(NO ₂) ₂] II (51-62)	146	
NaOH, H ₂ O ₂	I (55-D) + II (8-15)	146	
NaOH, K ₃ Fe(CN) ₆	I (36-55-D) + II (6-15)	146	
NaOH, AgNO ₃	I (30-D) + II (11)	146	
1. NaOH, CuCl ₂ , NH ₄ OH 2. 100°	I (90-D) + II (4)	146	
C ₂ H ₅ CD ₂ NO ₂	1. OH ⁻ 2. H ⁺	C ₂ H ₅ CDO (—)	250
CH ₂ =CHCH ₂ NO ₂	1. NaOH 2. H ₂ SO ₄	CH ₂ =CHCHO (76)	251
(CH ₃ O) ₂ P(O)CH(CH ₃)CH ₂ NO ₂	1. NaOCH ₃ 2. O ₃ , DMS	(CH ₃ O) ₂ P(O)CH(CH ₃)CHO (38)	252
CH ₂ =C(NO ₂)CH ₃	1. CH ₃ CH=C(OTMS)OCH ₃ , TiCl ₄ , Ti(OC ₃ H ₇ - <i>i</i>) ₄ 2. H ₂ O, heat	CH ₃ COCH ₂ CH(CH ₃)CO ₂ CH ₃ (64)	167, 168

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)


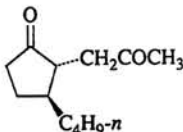

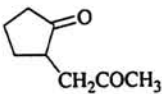
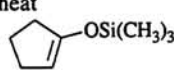

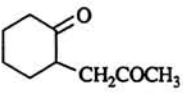



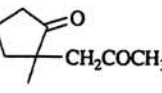

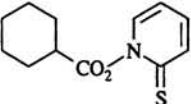
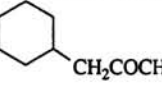
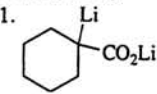
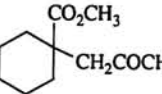
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
1. 		 (66)	253
2. $n\text{-C}_4\text{H}_9\text{Cu}[\text{P}(\text{C}_4\text{H}_9)_3]_2$ 3. HCl			
1. 	1. SnCl_4	 (63-70)	167, 168
2. H_2O , heat	1. TiCl_4 , 	" (61)	169 167
2. H_2O , heat	1. $(\text{CH}_3)_2\text{C}=\text{C}(\text{OTMS})\text{OCH}_3$, TiCl_4 , $\text{Ti}(\text{OC}_3\text{H}_7)_4$	$\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{CO}_2\text{CH}_3$ (66)	167
2. H_2O , heat	1. $n\text{-C}_4\text{H}_9\text{CH}(\text{Li})\text{CO}_2\text{Li}$, -100° 2. dil HCl	$\text{CH}_3\text{COCH}_2\text{CH}(\text{CO}_2\text{H})\text{C}_4\text{H}_9$ (65)	37
2. H_2O , heat	1. $n\text{-C}_4\text{H}_9\text{CH}(\text{Li})\text{CO}_2\text{Li}$, -100° 2. dil HCl; CH_3N_2	$\text{CH}_3\text{COCH}_2\text{CH}(\text{CO}_2\text{CH}_3)\text{C}_4\text{H}_9$ (65)	254
2. H_2O , heat	1. $n\text{-C}_3\text{H}_7\text{C}(\text{CH}_3)(\text{Li})\text{CO}_2\text{Li}$, -100° 2. dil HCl	$\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{H})\text{C}_3\text{H}_7$ (46)	37
2. H_2O , heat	1. $n\text{-C}_3\text{H}_7\text{C}(\text{CH}_3)(\text{Li})\text{CO}_2\text{Li}$, -100° 2. dil HCl; CH_3N_2	$\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{CH}_3)\text{C}_3\text{H}_7$ (46)	252
1. 	1. SnCl_4	 (61-85)	164, 166-168
2. H_2O , heat	1. 	" (83)	167
2. H_2O , heat	1. 	" (70)	167
2. H_2O , heat	1. 	 (41-60)	164, 167, 168
2. H_2O , heat	1. 	" (53)	167
2. H_2O , heat	1. $\text{CH}_2=\text{CHC}(\text{CH}_3)=\text{C}(\text{OTMS})\text{OCH}_3$, TiCl_4 , $\text{Ti}(\text{OC}_3\text{H}_7)_4$	$\text{CH}_3\text{COCH}_2\text{C}(\text{CO}_2\text{CH}_3)(\text{CH}_3)\text{CH}=\text{CH}_2$ (47)	165, 167, 168
2. H_2O , heat	1. $n\text{-C}_3\text{H}_7\text{C}(\text{Li})(\text{CH}_3)\text{CO}_2\text{Li}$ 2. HCl	$\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{H})\text{C}_3\text{H}_7$ (46)	168
	$\text{CH}_3\text{COCH}(\text{CH}_3)\text{COCH}_3$, KF	$\text{CH}_3\text{COC}(\text{CH}_3)(\text{CO}_2\text{CH}_3)\text{CH}_2\text{COCH}_3$ + (13) $\text{CH}_3\text{COC}(\text{CH}_3)(\text{CO}_2\text{CH}_3)\text{CH}_2\text{CH}(\text{NO}_2)\text{CH}_3$ (17)	168 229
	AIBN, TiCl_3	 (83)	
1. 		 (37)	254

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

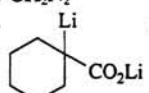
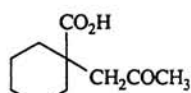

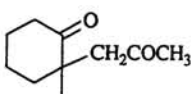


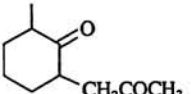

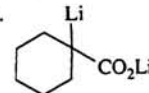
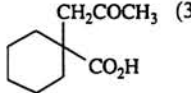
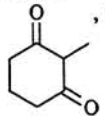
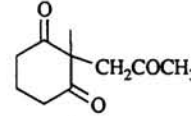
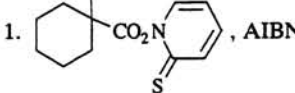
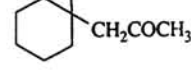
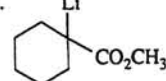
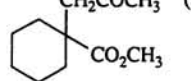
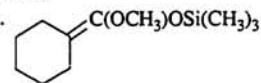
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	2. HCl 3. CH ₂ N ₂ 1.  , -100°	 (37)	37
	2. dil HCl 1. <i>n</i> -C ₄ H ₉ CH(Li)CO ₂ CH ₃ , -100° 2. dil HCl	CH ₃ COCH ₂ CH(CO ₂ CH ₃)C ₄ H ₉ - <i>n</i> (81)	37
	1.  , TiCl ₄	 (70)	164, 168
	2. H ₂ O, heat 1.  , SnCl ₄	" (60)	167
	2. H ₂ O, heat 1.  , SnCl ₄	 (63)	164, 168
	2. H ₂ O, heat 1.  , TiCl ₄	" (60)	167
	2. H ₂ O, heat 1. <i>n</i> -C ₅ H ₁₁ CH(Li)CO ₂ Li 2. HCl	CH ₃ COCH ₂ CH(CO ₂ H)C ₅ H ₁₁ - <i>n</i> (65)	168
	1. 	 (37)	168
	2. HCl 1. <i>n</i> -C ₄ H ₉ CH(Li)CO ₂ CH ₃ 2. HCl	CH ₃ COCH ₂ CH(CO ₂ CH ₃)C ₄ H ₉ - <i>n</i> (81)	168
	2. HCl 1.  , KF	 (14-96)	168
	1.  , AIBN	 (55)	229
	2. TiCl ₄ 1. C ₆ H ₅ CH(Li)CO ₂ Li 2. HCl	CH ₃ COCH ₂ CH(C ₆ H ₅)CO ₂ H (88)	37, 168
	1. C ₆ H ₅ CH(Li)CO ₂ Li 2. HCl	CH ₃ COCH ₂ CH(C ₆ H ₅)CO ₂ CH ₃ (88)	254
	3. CH ₂ N ₂ 1. C ₆ H ₅ SCH(Li)CO ₂ Li 2. HCl	CH ₃ COCH ₂ CH(SC ₆ H ₅)CO ₂ H (80)	37, 168, 254
	1. C ₆ H ₅ SCH(Li)CO ₂ Li 2. HCl	CH ₃ COCH ₂ CH(SC ₆ H ₅)CO ₂ CH ₃ (50-80)	254
	3. CH ₂ N ₂ 1. 	 (53)	37, 168
	2. HCl 1. 	" (79)	165, 167

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

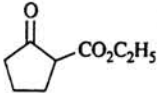
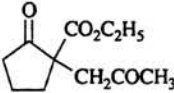
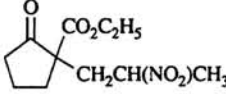
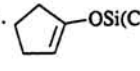
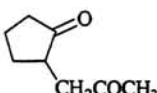
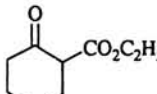
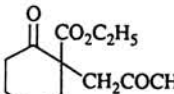
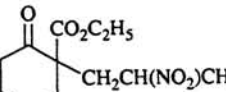
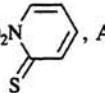
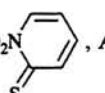




Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	2. TiCl_4 , $\text{Ti}(\text{OC}_3\text{H}_7)_4$ 3. H_2O , heat		
	1. $\text{CH}_2=\text{C}(\text{OTMS})\text{C}_6\text{H}_{13-n}$, SnCl_4 2. H_2O , heat	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COC}_6\text{H}_{13-n}$ (65)	164, 168
	1. $\text{CH}_2=\text{C}(\text{OTMS})\text{C}_6\text{H}_{13-n}$, TiCl_4 2. H_2O , heat	" (63)	167
	, KF		
		 (20)	168
		+  (47)	
	1. $n\text{-C}_8\text{H}_{17}\text{CH}(\text{Li})\text{CO}_2\text{CH}_3$ 2. HCl	$\text{CH}_3\text{COCH}_2\text{CH}(\text{CO}_2\text{CH}_3)\text{C}_8\text{H}_{17-n}$ (61)	37
	1. $n\text{-C}_8\text{H}_9\text{CH}=\text{C}(\text{OCH}_3)\text{OTMS}$, TiCl_4 , $\text{Ti}(\text{OC}_3\text{H}_7)_4$ 2. H_2O , heat	" (84)	165, 167, 168
	1.  , SnCl_4	 (63-70)	164, 167, 168
	2. H_2O , heat		
	1. $\text{C}_6\text{H}_5\text{CH}(\text{Li})\text{CO}_2\text{CH}_3$ 2. HCl	$\text{CH}_3\text{COCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CO}_2\text{CH}_3$ (79)	37, 168
	1. $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{OCH}_3)\text{OTMS}$, TiCl_4 , $\text{Ti}(\text{OC}_3\text{H}_7)_4$ 2. H_2O , heat	$\text{CH}_3\text{COCH}_2\text{CH}(\text{CO}_2\text{CH}_3)\text{C}_6\text{H}_5$ (82)	165, 167, 168
	1. $\text{C}_6\text{H}_5\text{SCH}(\text{Li})\text{CO}_2\text{CH}_3$ 2. HCl	$\text{C}_6\text{H}_5\text{SCH}(\text{CO}_2\text{CH}_3)\text{CH}_2\text{COCH}_3$ (65)	37, 168
	1. $\text{C}_6\text{H}_5\text{SC}(\text{Li})(\text{CH}_3)\text{CO}_2\text{Li}$ 2. HCl	$\text{CH}_3\text{COCH}_2\text{C}(\text{SC}_6\text{H}_5)(\text{CH}_3)\text{CO}_2\text{H}$ (55)	37, 168
	1. $\text{C}_6\text{H}_5\text{SC}(\text{Li})(\text{CH}_3)\text{CO}_2\text{Li}$ 2. HCl 3. CH_2N_2	$\text{CH}_3\text{COCH}_2\text{C}(\text{SC}_6\text{H}_5)(\text{CH}_3)\text{CO}_2\text{CH}_3$ (55)	254
	, KF		
		 (11)	168
		+  (30)	
	1. $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{CO}_2\text{N}$  , AIBN	$(\text{C}_6\text{H}_5)_2\text{CH}(\text{CH}_2)_2\text{COCH}_3$ (81)	229
	2. TiCl_3		
	1. $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{CHCO}_2\text{N}$  , AIBN	$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{CHCH}_2\text{COCH}_3$ (75)	229
	2. TiCl_3		
	1. $\text{CH}_2=\text{CHCOCH}_3$, Al_2O_3	 (62)	245
			
	2. H_2O_2 , K_2CO_3		
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}(\text{CH}_3)\text{CH}_2\text{NO}_2$	1. NaOCH_3 , CH_3OH 2. O_3 , DMS	$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}(\text{CH}_3)\text{CHO}$ (90)	255
	1. NaOCH_3 , CH_3OH 2. Rose Bengal, O_2 , $h\nu$	" (90)	256
C_4			
	1. NaOH	 (56-D)	10

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
<i>n</i> -C ₄ H ₉ NO ₂	2. HCl 1. KOH, MgSO ₄ 2. KMnO ₄	" (94-D)	124
	1. NaOH 2. H ₂ SO ₄	<i>n</i> -C ₃ H ₇ CHO (85)	21
	1. Ca(OH) ₂ 2. H ₂ SO ₄	" (85)	21
	1. KOH, MgSO ₄ 2. KMnO ₄	" (83-97-D)	124
	NaOH, 8-azaflavin (28) 1. H ₂ O ₂ 2. K ₂ CO ₃ , H ₂ O 3. HCl	" (—) " (76)	139 147
	NaOH, (NH ₄) ₂ S ₂ O ₈	" (18-27) + <i>n</i> -C ₃ H ₇ C(NO ₂)=CHC ₃ H ₇ - <i>n</i> (32)	150
C ₂ H ₅ CH(NO ₂)CH ₃	1. NaOH 2. H ₂ SO ₄	C ₂ H ₅ COCH ₃ (82)	21
	1. Ca(OH) ₂ 2. H ₂ SO ₄	" (86)	21
	1. KOH, MgSO ₄ 2. KMnO ₄	" (94-D)	124
	1. H ₂ O ₂ 2. K ₂ CO ₃ , H ₂ O 3. HCl NaOH, Na ₂ S ₂ O ₈	" (81) " (48-D) + C ₂ H ₅ C(CH ₃)(NO ₂)C(CH ₃)- (NO ₂)C ₂ H ₅ (37)	147 146
<i>i</i> -C ₄ H ₉ NO ₂	1. NaOH 2. H ₂ SO ₄	<i>i</i> -C ₃ H ₇ CHO (32)	21
	1. Ca(OH) ₂ 2. H ₂ SO ₄	" (36)	21
	1. KOH, MgSO ₄	" (73-D)	124
<i>t</i> -C ₄ H ₉ NO ₂ HOCH ₂ CH(NO ₂)C ₂ H ₅	2. KMnO ₄ NaOH, (NH ₄) ₂ S ₂ O ₈	" (20) + <i>i</i> -C ₃ H ₇ CH(NO ₂)CH(NO ₂)C ₃ H ₇ - <i>i</i> (10)	150
	TiCl ₃ , H ₂ O, heat 1. OH ⁻ 2. H ⁺	(CH ₃) ₂ CO (—, D) HOCH ₂ COC ₂ H ₅ I (—) + HOCH ₂ C(=NOH)C ₂ H ₅ II (—) + CH ₂ =C(NO ₂)C ₂ H ₅ III (—)	155 105
O ₂ N(CH ₂) ₄ NO ₂	1. OH ⁻ 2. HCl H ₂ SO ₄	I (50) + III (20)	257
	1. ZnCl ₂ , HCl 2. H ₂ O	I (50) + III (20) OHC(CH ₂) ₂ CHO (—)	258 183
CH ₃ CH=CHCH ₂ NO ₂	1. NaOH 2. H ₂ SO ₄	CH ₃ CH=CHCHO (68)	251
O ₂ NCH ₂ CH=CHCH ₂ NO ₂	1. NaOH 2. H ₂ SO ₄	OHCCH=CHCHO (58)	251
(CH ₃ O) ₂ P(O)CH(C ₂ H ₅)CH ₂ NO ₂	1. NaOCH ₃ 2. O ₃ , DMS	(CH ₃ O) ₂ P(O)CH(C ₂ H ₅)CHO (44)	252
CH ₃ O ₂ C(CH ₂) ₃ NO ₂	1. NaOCH ₃ 2. H ₂ SO ₄ , CH ₃ OH	CH ₃ O ₂ C(CH ₂) ₂ CH(OCH ₃) ₂ (84)	258
CH ₂ =C(NO ₂)C ₂ H ₅	1. CH ₃ CH=C(OTMS)OCH ₃ , TiCl ₄ , Ti(OC ₃ H ₇ - <i>i</i>) ₄ 2. H ₂ O, heat	C ₂ H ₅ COCH ₂ CH(CH ₃)CO ₂ CH ₃ (63)	165, 167
	1. (CH ₃) ₂ C=C(OTMS)OCH ₃ , TiCl ₄ , Ti(OC ₃ H ₇ - <i>i</i>) ₄ 2. H ₂ O, heat	C ₂ H ₅ COCH ₂ C(CH ₃) ₂ CO ₂ CH ₃ (68)	167, 168
	1. <i>n</i> -C ₄ H ₉ CH(Li)CO ₂ Li, -100° 2. dil HCl	C ₂ H ₅ COCH ₂ CH(C ₄ H ₉ - <i>n</i>)CO ₂ H (55)	37
	1. <i>n</i> -C ₄ H ₉ CH(Li)CO ₂ Li, -100° 2. dil HCl	C ₂ H ₅ COCH ₂ CH(C ₄ H ₉ - <i>n</i>)CO ₂ CH ₃ (55)	254
	3. CH ₂ N ₂ 1. <i>n</i> -C ₃ H ₇ C(CH ₃)(Li)CO ₂ Li, -100° 2. dil HCl	C ₂ H ₅ COCH ₂ C(CH ₃)(C ₃ H ₇ - <i>n</i>)CO ₂ H (38)	37
	1. <i>n</i> -C ₃ H ₇ C(CH ₃)(Li)CO ₂ Li, -100° 2. dil HCl 3. CH ₂ N ₂	C ₂ H ₅ COCH ₂ C(CH ₃)(C ₃ H ₇ - <i>n</i>)CO ₂ CH ₃ (38)	254

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)


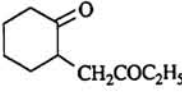

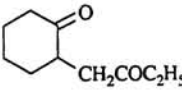

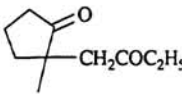
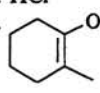
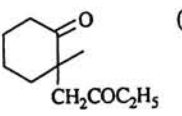
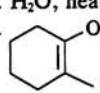
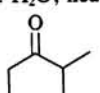
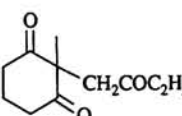
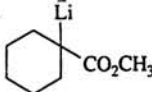
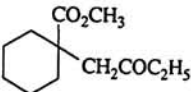

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
1. 	1. TiCl_4	 (76)	164, 168
2. H_2O	1. 	 (62)	167
2. H_2O	1. 	 (41)	164, 168
2. H_2O	1. $n\text{-C}_6\text{H}_9\text{CH}(\text{Li})\text{CO}_2\text{CH}_3$	$\text{C}_2\text{H}_5\text{COCH}_2\text{CH}(\text{CO}_2\text{CH}_3)\text{C}_6\text{H}_9\text{-}n$ (56)	37
2. HCl	1. 	 (62-82)	164, 167
2. H_2O , heat	1. 	" (82)	167, 168
2. H_2O , heat	1.  , KF	 (96)	168
1. $\text{C}_6\text{H}_5\text{CH}(\text{Li})\text{CO}_2\text{Li}$	2. HCl	$\text{C}_2\text{H}_5\text{COCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CO}_2\text{H}$ (73)	37
1. $\text{C}_6\text{H}_5\text{CH}(\text{Li})\text{CO}_2\text{Li}$	2. HCl	$\text{C}_2\text{H}_5\text{COCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CO}_2\text{CH}_3$ (73)	254
3. CH_2N_2	1. $\text{C}_6\text{H}_5\text{SCH}(\text{Li})\text{CO}_2\text{Li}$	$\text{C}_2\text{H}_5\text{COCH}_2\text{CH}(\text{SC}_6\text{H}_5)\text{CO}_2\text{H}$ (76)	37
2. HCl	1. $\text{C}_6\text{H}_5\text{SCH}(\text{Li})\text{CO}_2\text{Li}$	$\text{C}_2\text{H}_5\text{COCH}_2\text{CH}(\text{SC}_6\text{H}_5)\text{CO}_2\text{CH}_3$ (76)	254
3. CH_2N_2	1. 	 (41)	37
2. HCl	1. 	" (78)	167
2. H_2O , heat	1. $\text{C}_6\text{H}_5\text{CH}(\text{Li})\text{CO}_2\text{CH}_3$	$\text{C}_2\text{H}_5\text{COCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CO}_2\text{CH}_3$ (75)	37
2. HCl	1. $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{OCH}_3)\text{OTMS}$, TiCl_4 , $\text{Ti}(\text{OC}_3\text{H}_7\text{-}i)_4$	" (74)	167
2. H_2O , heat	1. $\text{C}_6\text{H}_5\text{SCH}(\text{Li})\text{CO}_2\text{CH}_3$	$\text{C}_2\text{H}_5\text{COCH}_2\text{CH}(\text{SC}_6\text{H}_5)\text{CO}_2\text{CH}_3$ (66)	37
2. HCl	1. $\text{C}_6\text{H}_5\text{SC}(\text{Li})(\text{CH}_3)\text{CO}_2\text{Li}$	$\text{C}_2\text{H}_5\text{COCH}_2\text{C}(\text{CH}_3)(\text{SC}_6\text{H}_5)\text{CO}_2\text{H}$ (39)	37
2. HCl	1. $\text{C}_6\text{H}_5\text{SC}(\text{Li})(\text{CH}_3)\text{CO}_2\text{Li}$	$\text{C}_2\text{H}_5\text{COCH}_2\text{C}(\text{CH}_3)(\text{SC}_6\text{H}_5)\text{CO}_2\text{CH}_3$ (39)	254
3. CH_2N_2	1. $n\text{-C}_8\text{H}_{17}\text{CH}(\text{Li})\text{CO}_2\text{CH}_3$	$\text{C}_2\text{H}_5\text{COCH}_2\text{CH}(\text{CO}_2\text{CH}_3)\text{C}_8\text{H}_{17}\text{-}n$ (53)	37
2. HCl	1. $n\text{-C}_8\text{H}_{17}\text{CH}=\text{C}(\text{OTMS})\text{OCH}_3$, TiCl_4 , $\text{Ti}(\text{OC}_3\text{H}_7\text{-}i)_4$	" (81)	167
2. H_2O , heat			

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)


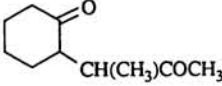

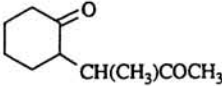



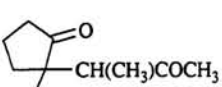

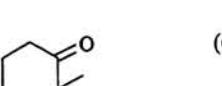

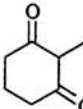

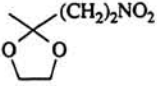
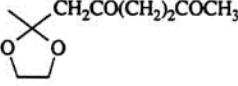
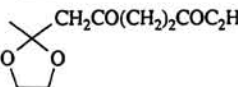

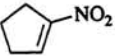


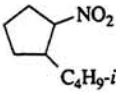
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
$\text{CH}_3\text{CH}=\text{C}(\text{NO}_2)\text{CH}_3$	1.  $\text{OSi}(\text{CH}_3)_3$, AlCl_3 2. H_2O , heat	 (63)	164, 168
	1.  $\text{OSi}(\text{CH}_3)_3$, AlCl_3 2. H_2O , heat	 (63)	167
	1.  $\text{OSi}(\text{CH}_3)_3$, SnCl_4 2. H_2O , heat	" (50)	167
	1.  $\text{OSi}(\text{CH}_3)_3$, TiCl_4 2. H_2O , heat	" (41)	167
	1.  $\text{OSi}(\text{CH}_3)_3$, SnCl_4 2. H_2O , heat	 (36)	167
	1.  $\text{OSi}(\text{CH}_3)_3$, SnCl_4 2. H_2O , heat	 (63-71)	164, 167
	1.  $\text{OSi}(\text{CH}_3)_3$, TiCl_4 2. H_2O , heat	" (71)	168 167
	 , KF	 (63)	168
	1. $\text{C}_6\text{H}_5\text{SCH}(\text{Li})\text{CO}_2\text{Li}$ 2. HCl	$\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}(\text{SC}_6\text{H}_5)\text{CO}_2\text{H}$ (64)	37, 168
	1. $\text{C}_6\text{H}_5\text{SCH}(\text{Li})\text{CO}_2\text{Li}$ 2. HCl 3. CH_2N_2	$\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}(\text{SC}_6\text{H}_5)\text{CO}_2\text{CH}_3$ (64)	254
	1. $\text{CH}_2=\text{CHCOCH}_3$, Al_2O_3 2. H_2O_2 , K_2CO_3	 (80)	245
	1. $\text{CH}_2=\text{CHCO}_2\text{H}$, Al_2O_3 2. H_2O_2 , K_2CO_3	 (68)	245
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{NO}_2$	1. NaOCH_3 , CH_3OH 2. O_3 , DMS	$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}(\text{C}_2\text{H}_5)\text{CHO}$ (99)	255
	1. NaOCH_3 , CH_3OH 2. Rose Bengal, O_2 , $h\nu$	" (90)	256
C_5  	1. NaOH 2. HCl	 (89-D)	10
	NaOH , 8-azaflavin (28) 1. $(i\text{-C}_4\text{H}_9)_3\text{Al}$ 2. $(\text{C}_2\text{H}_5)_2\text{O}$ 3. HCl , 0°	 I (6) +  II (86)	139 260
	1. $(i\text{-C}_4\text{H}_9)_3\text{Al}$ 2. $(\text{C}_2\text{H}_5)_2\text{O}$ 3. HCl , rt	I (58) + II (21)	260

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

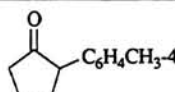

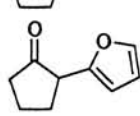

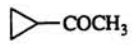
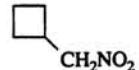
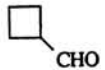
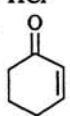
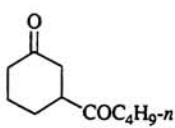


Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. $C_6H_5CH_3$, $TiCl_4$ 2. H_3O^+	 (90)	261
	1.  , $TiCl_4$ 2. H_3O^+	 (76)	261
	1. $NaOH$ 2. HCl	 (64-D)	10
	1. KOH , $MgSO_4$ 2. $KMnO_4$	" (77-D)	124
 $n-C_3H_7NO_2$	1. KOH , $MgSO_4$ 2. $KMnO_4$	 (91-D)	124
	1. H_2O_2 2. K_2CO_3 , H_2O 3. HCl	$n-C_4H_9CHO$ (81)	147
	1.  , Al_2O_3 2. H_2O_2 , K_2CO_3 1. $CH_2=CHCO_2C_2H_5$, Al_2O_3 2. H_2O_2 , K_2CO_3 $CH_2=C(CH_3)CO_2CH_3$, CH_3CN , $C_6H_5N=NC_6H_5$, e^-	 (55)	245
$n-C_5H_{11}NO_2$		$n-C_4H_9CO(CH_2)_2CO_2C_2H_5$ (90)	245
$C_2H_5CH=C(NO_2)CH_3$	$CH_2=C(CH_3)CO_2CH_3$, CH_3CN , $C_6H_5N=NC_6H_5$, e^- 1. $(n-C_4H_9)_3SnH$ 2. MCPBA	$n-C_4H_9COCH_2CH(CH_3)CO_2CH_3$ (62)	194
		$C_2H_5COCH_3$ (72)	228a
$i-C_3H_7CH(NO_2)CH_3$	1. KOH , $MgSO_4$ 2. $KMnO_4$	$i-C_3H_7COCH_3$ (94-D)	124
$t-C_4H_9CH_2NO_2$ $HO(CH_2)_3CH(NO_2)CH_3$	"	$t-C_4H_9CHO$ (63-69-D) $HO(CH_2)_3COCH_3$ (37-D)	124 35
$CH_3CH(NO_2)(CH_2)_2CO_2H$	1. $NaOH$ 2. H_2SO_4	$CH_3CO(CH_2)_2CO_2H$ (—)	87
$CH_3CH(NO_2)CO_2C_2H_5$	1. $NaOH$ or Py 2. H^+	$CH_3CO(CH_2)_2CO_2H$ (—)	87
$CH_3CH(NO_2)CO_2C_2H_5$	1. $(C_2H_5)_3N$ 2. $MoO_5 \cdot Py \cdot HMPA$	$CH_3COCO_2C_2H_5$ (73)	145
$CH_3CH(NO_2)(CH_2)_2CN$	$TiCl_3$, H_2O 1. $NaOH$ 2. $TiCl_3$, NH_4OAc , H_2O	$CH_3CO(CH_2)_2CN$ (55) " (90)	154 156
$O_2N(CH_2)_5NO_2$	1. $NaOH$ 2. $TiCl_3$, NH_4OAc , H_2O	$OHC(CH_2)_3CHO$ (—)	183
$CH_3CO(CH_2)_3NO_2$	1. $ZnCl_2$, HCl 2. H_2O	$OHC(CH_2)_3CHO$ (—)	183
$CH_3CH(NO_2)(CH_2)_2CO_2C_2H_5$	1. $(C_2H_5)_3N$ 2. $n-C_{16}H_{33}N(CH_3)_3^+MnO_4^-$	$CH_3CO(CH_2)_2CHO$ (57)	262
	1. $NaOH$ 2. HCl	$CH_3CO(CH_2)_2CO_2H$ (40)	263
	1. $KOAc$, CH_3OH , e^- 2. H_3O^+	$CH_3CO(CH_2)_2CHO$ (54)	195
 $AcOCH_2CH=C(CH_3)CH_2NO_2$	Silica gel, $NaOCH_3$ 1. Fe , $HOAc$ 2. CH_2O , H^+	 $(CH_2)_2CHO$ (81) $AcOCH_2CH=C(CH_3)CHO$ (40)	200 185
$CH_3O_2CCH_2CH(CH_3)CH_2NO_2$	1. $NaOCH_3$, CH_3OH 2. H_2SO_4 , CH_3OH	$CH_3O_2CCH_2CH(CH_3)CH(OCH_3)_2$ (86)	258
$(CH_3O)_2P(O)CH(CH_2NO_2)C_3H_7-i$	1. $NaOCH_3$ 2. O_3 , DMS	$(CH_3O)_2P(O)CH(CHO)C_3H_7-i$ (35)	252
$(C_6H_5)_2P(O)CH(CH_2NO_2)C_3H_7-i$	1. $NaOCH_3$ 2. O_3 , DMS	$(C_6H_5)_2P(O)CH(CHO)C_3H_7-i$ (90)	255
	1. $NaOCH_3$, CH_3OH 2. Rose Bengal, O_2 , $h\nu$	" (91)	256

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

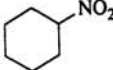
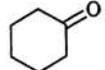
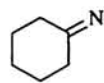
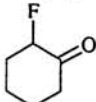
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
$(C_6H_5)_2P(O)CH(CH_2NO_2)C_3H_7-n$	1. NaOCH ₃ 2. Rose Bengal, O ₂ , hv	$(C_6H_5)_2P(O)CH(CHO)C_3H_7-n$ (97)	256
$\begin{array}{c} CH_2NO_2 \\ \\ CH_2 \\ \\ H-C-OAc \\ \\ H-C-OAc \\ \\ CH_2OAc \end{array}$	1. NaOH 2. H ₂ SO ₄	$\begin{array}{c} CHO \\ \\ CH_2 \\ \\ H-C-OH \\ \\ H-C-OH \\ \\ CH_2OH \end{array}$ (23-A)	264
$\begin{array}{c} CH_2NO_2 \\ \\ AcO-C-H \\ \\ H-C-OAc \\ \\ H-C-OAc \\ \\ CH_2OAc \end{array}$	1. NaOH 2. H ₂ SO ₄	$\begin{array}{c} CHO \\ \\ HO-C-H \\ \\ H-C-OH \\ \\ H-C-OH \\ \\ CH_2OH \end{array}$ (70-B)	264
$\begin{array}{c} CH_2NO_2 \\ \\ H-C-OAc \\ \\ H-C-OAc \\ \\ H-C-OAc \\ \\ CH_2OAc \end{array}$	1. NaOH 2. H ₂ SO ₄	$\begin{array}{c} CHO \\ \\ H-C-OH \\ \\ H-C-OH \\ \\ H-C-OH \\ \\ CH_2OH \end{array}$ (72-B)	264
$\begin{array}{c} CH_2NO_2 \\ \\ CH_2OAc \\ \\ CH_2NO_2 \\ \\ CH_2 \\ \\ H-C-OAc \\ \\ H-C-OAc \\ \\ CH_2OAc \end{array}$	1. NaOH 2. H ₂ SO ₄ 3. (C ₆ H ₅ CH ₂ N(C ₆ H ₅)NH ₂)	$\begin{array}{c} CHO \\ \\ CH_2OH \\ \\ CHO \\ \\ CH_2 \\ \\ H-C-OAc \\ \\ H-C-OAc \\ \\ CH_2OAc \end{array}$ (60-B)	265a
C ₆ 	1. NaOH 2. HCl	 (97-D)	10
	1. OH ⁻ 2. H ⁺	" (85-90)	16
	1. OH ⁻ 2. KMnO ₄	" (100)	116
	1. KOH, CH ₃ OH 2. KMnO ₄ , MgSO ₄	" (93)	131
	1. KOC ₄ H ₉ -t 2. t-C ₄ H ₉ O ₂ H, VO(acac) ₂	" (86)	144
	1. LDA 2. MoO ₅ ·Py·HMPA	" (86)	145
	1. (C ₂ H ₅) ₃ N 2. MoO ₅ ·Py·HMPA	" (81)	145
	NaOH, Na ₂ S ₂ O ₈	" (66-D)	146
	1. HCl, DMF 2. VCl ₂ , H ₂ O, NaOH	" (53)	170
	1. H ₂ O ₂ 2. K ₂ CO ₃ , H ₂ O 3. HCl	" (88)	147
	1. (C ₂ H ₅) ₃ N 2. CAN	" (80)	148
	1. TMSCl, Li ₂ S 2. CAN	" (92)	148
	(n-C ₄ H ₉) ₄ N ⁺ Br ⁻ , CH ₃ CN, O ₂ , e ⁻	" (70)	194
	NaNO ₂ , n-C ₃ H ₇ ONO, DMSO	" (67)	197
	Silica gel, NaOCH ₃	" (99)	200
	1. (C ₂ H ₅) ₃ N 2. C ₁₆ H ₃₃ N(CH ₃) ₃ ⁺ MnO ₄ ⁻	" (80)	261
	1. NaOH 2. H ₂ SO ₄ , Na ₂ SO ₄	" (66) +  (23)	266
	DBU, TMSCl, MCPBA (C ₂ H ₅) ₃ N, CAN	" (96)  (80)	143b 148

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

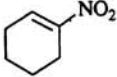
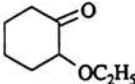
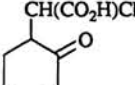
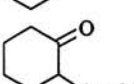
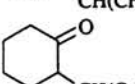
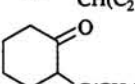
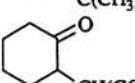
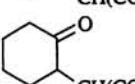
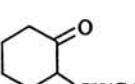
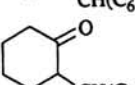
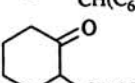
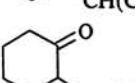
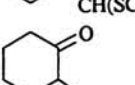
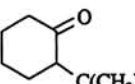
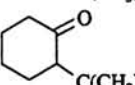
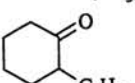
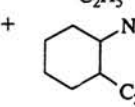
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. TMSCl, Li ₂ S 2. CAN	" (90)	148
	1. LiHB(C ₄ H ₉ -s) ₃ 2. H ₂ SO ₄	" (81)	224
	1. C ₂ H ₅ OH, SnCl ₂ 2. H ⁺	 (79)	221
	1. CH ₃ CH(Li)CO ₂ Li, -100° 2. dil HCl	 (43)	37
	1. CH ₃ CH=C(OTMS)OCH ₃ , TiCl ₄ , Ti(OC ₂ H ₅ -i) ₄ 2. H ₂ O, heat	 (70)	165, 167, 168
	1. C ₂ H ₅ CH(Li)CO ₂ Li 2. HCl	 (43)	168
	1. (CH ₃) ₂ C=C(OTMS)OCH ₃ , TiCl ₄ , Ti(OC ₂ H ₅ -i) ₄ 2. H ₂ O, heat	 (25)	165, 167, 168
	1. n-C ₄ H ₉ CH(Li)CO ₂ Li 2. HCl	 (24)	37
	1. n-C ₄ H ₉ CH(Li)CO ₂ Li 2. HCl 3. CH ₂ N ₂	 (24)	254
	1. n-C ₄ H ₉ CH(Li)CO ₂ CH ₃ 2. HCl	" (54)	37, 168
	1. C ₆ H ₅ CH(Li)CO ₂ Li 2. HCl	 (72)	37, 168
	1. C ₆ H ₅ CH(Li)CO ₂ Li 2. HCl 3. CH ₂ N ₂	 (72)	254
	1. C ₆ H ₅ CH(Li)CO ₂ CH ₃ 2. HCl	 (61)	37, 168
	1. C ₆ H ₅ SCH(Li)CO ₂ Li 2. HCl	 (72)	37, 168
	1. C ₆ H ₅ SCH(Li)CO ₂ Li 2. HCl 3. CH ₂ N ₂	 (76)	254
1. C ₆ H ₅ SCH(Li)CO ₂ CH ₃ 2. HCl	" (52)	37, 168	
1. C ₆ H ₅ SC(Li)(CH ₃)CO ₂ Li 2. HCl	 (37)	37, 168	
1. C ₆ H ₅ SC(Li)(CH ₃)CO ₂ Li 2. HCl 3. CH ₂ N ₂	 (37)	254	
1. (C ₂ H ₅) ₃ Al 2. (C ₂ H ₅) ₂ O 3. HCl, 0°	 (16-21) +  (67-75)	259	

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

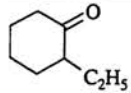
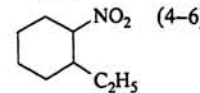
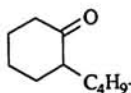
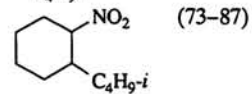
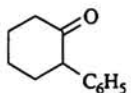
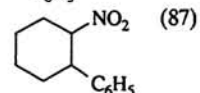
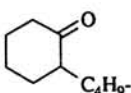
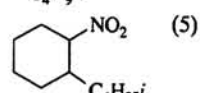
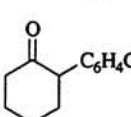
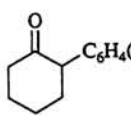
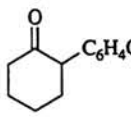

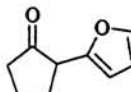
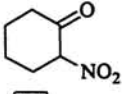
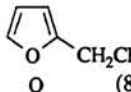
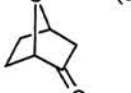
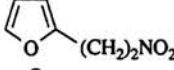


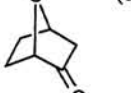
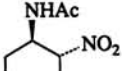
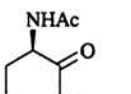
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. (C ₂ H ₅) ₃ Al 2. (C ₂ H ₅) ₂ O 3. HCl, rt	 (83-86) +  (4-6)	259
	1. (<i>i</i> -C ₄ H ₉) ₃ Al 2. (C ₂ H ₅) ₂ O 3. HCl, 0°	 (4-12) +  (73-87)	259
	1. (C ₆ H ₅) ₃ Al 2. (C ₂ H ₅) ₂ O 3. HCl, 0°	 (6) +  (87)	259
	1. (<i>i</i> -C ₄ H ₉) ₃ Al 2. (C ₂ H ₅) ₂ O 3. HCl, rt	 (82) +  (5)	259
	1. C ₆ H ₅ CH ₃ , TiCl ₄ 2. H ₃ O ⁺	 (94)	260
	1. C ₆ H ₅ C ₄ H ₉ - <i>t</i> , TiCl ₄ 2. H ₃ O ⁺	 (86)	260
	1. C ₆ H ₅ OCH ₃ , TiCl ₄ 2. H ₃ O ⁺	 (90)	260
	1.  , TiCl ₄ 2. H ₃ O ⁺ H ₂ O ₂ , K ₂ CO ₃ , CH ₃ OH	 (72) HO ₂ C(CH ₂) ₄ CO ₂ H (86)	260 266a
	1. NaOH, C ₂ H ₅ OH 2. H ₂ SO ₄ , H ₂ O, C ₃ H ₁₂	 (47)  (80)	267 268
  	1. OH ⁻ 2. H ⁺		269
 <i>n</i> -C ₄ H ₉ CH(NO ₂)CH ₃	1. KOH, MgSO ₄ 2. KMnO ₄	 (70) <i>n</i> -C ₄ H ₉ COCH ₃ (82)	269 147
<i>t</i> -C ₄ H ₉ CH(NO ₂)CH ₃	1. H ₂ O ₂ 2. K ₂ CO ₃ , H ₂ O 3. HCl 1. KOH, MgSO ₄ 2. KMnO ₄	<i>t</i> -C ₄ H ₉ COCH ₃ (66-D)	124

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

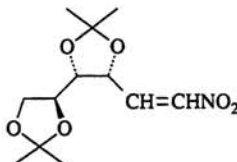
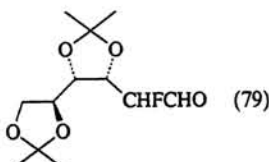
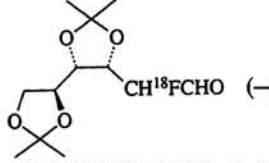
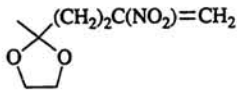
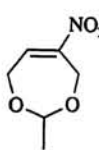
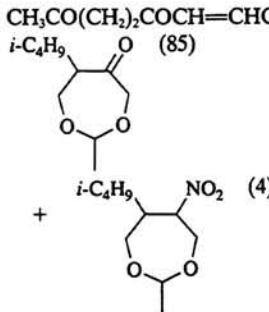
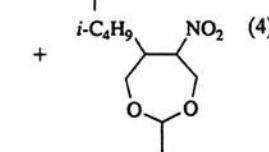
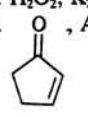
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
$\text{CH}_3\text{CH}(\text{NO}_2)(\text{CH}_2)_2\text{CH}=\text{CH}_2$	1. NaOH, CH_3OH 2. Rose Bengal, O_2 , $h\nu$	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CH}=\text{CH}_2$ (66)	140
	1. H_2O_2 , NaHCO_3 2. KHF_2 , $\text{HO}(\text{CH}_2)_2\text{OH}$, heat	 (79)	235a
	1. H_2O_2 , NaHCO_3 2. KH^{18}F_2 , heat	 (—)	235b
	1. $(i\text{-C}_4\text{H}_9)_3\text{Al}$ 2. HCl	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COC}_5\text{H}_{11}\text{-}i$ (91)	270
	1. $(\text{C}_6\text{H}_5)_3\text{Al}$ 2. HCl	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COCH}_2\text{C}_6\text{H}_5$ (93)	270
	$(i\text{-C}_4\text{H}_9)_2\text{AlCH}=\text{CHC}_4\text{H}_9\text{-}n$	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COCH}=\text{CHC}_4\text{H}_9\text{-}n$ (96)	270
	1. $(i\text{-C}_4\text{H}_9)_3\text{Al}$ 2. NaOH, H_2O 3. C_6H_{14} 4. KMnO_4 5. NaHSO_3	 (85) +  (4)	259
$\text{CH}_2=\text{C}(\text{NO}_2)\text{C}_4\text{H}_9\text{-}n$	1. $\text{C}_6\text{H}_5\text{CH}_3$, TiCl_4 2. H_3O^+	$n\text{-C}_4\text{H}_9\text{COCH}_2\text{C}_5\text{H}_4\text{CH}_3\text{-}4$ (62)	260
$n\text{-C}_6\text{H}_{13}\text{NO}_2$	1. H_2O_2 2. K_2CO_3 , H_2O 3. HCl TiCl_3 , NH_4OAc , H_2O	$n\text{-C}_5\text{H}_{11}\text{CHO}$ (80)	147
	1. NaOCH_3	" (45)	154
	2. TiCl_3 , NH_4OAc , H_2O	" (45)	156
	1. $\text{CH}_2=\text{CHCOCH}_3$, Al_2O_3 2. H_2O_2 , K_2CO_3	$\text{C}_5\text{H}_{11}\text{CO}(\text{CH}_2)_2\text{COCH}_3$ (71)	245
	1.  , Al_2O_3	(58)	245
	2. H_2O_2 , K_2CO_3	$n\text{-C}_5\text{H}_{11}\text{CO}(\text{CH}_2)_2\text{COC}_2\text{H}_5$ (78)	245
$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CH}(\text{NO}_2)\text{CH}_3$	1. $\text{CH}_2=\text{CHCO}_2\text{H}_5$, Al_2O_3 2. H_2O_2 , K_2CO_3 $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{Br}^-$, CH_3CN , O_2 , e^- Silica gel, NaOCH_3 Silica gel, KMnO_4	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COCH}_3$ (82–86)	194
	1. $(\text{C}_2\text{H}_5)_3\text{N}$	" (55–81)	202, 203
	2. $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3^+\text{MnO}_4^-$	" (82)	202
$\text{CH}_3\text{CH}(\text{NO}_2)(\text{CH}_2)_2\text{CO}_2\text{CH}_3$	TiCl_3 , H_2O	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CO}_2\text{H}$ (40)	154
$i\text{-C}_3\text{H}_7\text{CHOHCH}(\text{NO}_2)\text{CH}_3$	TiCl_3 , NH_4OAc , H_2O H_2SO_4	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CO}_2\text{CH}_3$ (35)	154
	1. OH^-	$i\text{-C}_3\text{H}_7\text{CHOHCOCH}_3$ I (50) + $i\text{-C}_3\text{H}_7\text{CH}=\text{C}(\text{NO}_2)\text{CH}_3$ II (10)	257
	2. HCl	I (50) + II (10)	257
$\text{CH}_3\text{CH}(\text{NO}_2)(\text{CH}_2)_2\text{CHOHCH}_3$	1. $(\text{C}_2\text{H}_5)_3\text{N}$ 2. $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3^+\text{MnO}_4^-$	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CHOHCH}_3$ (62)	261
$\text{CH}_3\text{COCH}=\text{CHCH}(\text{NO}_2)\text{CH}_3$	1. KOH 2. $(\text{CH}_3\text{O})_2\text{SO}_2$, heat	$\text{CH}_3\text{COCH}=\text{CHCOCH}_3$ (80)	151

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)



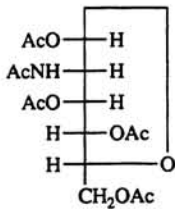
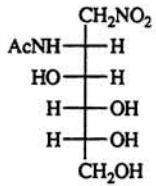

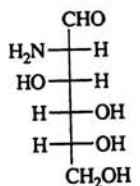
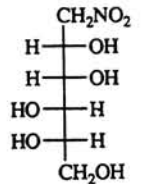
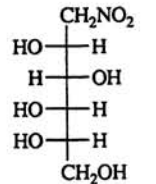
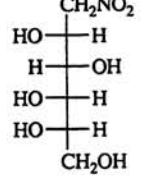

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
$\text{CH}_3\text{COCH}=\text{CHC}(\text{CH}_3)=\text{NO}_2\text{Na}$	Silica gel, CH_3OH	" (36)	152
$\text{OHCC}(\text{CH}_3)=\text{CHC}(\text{CH}_3)=\text{NO}_2\text{Na}$	Silica gel, CH_3OH	$\text{OHCC}(\text{CH}_3)=\text{CHCOCH}_3$ (38)	152
$(\text{C}_2\text{H}_5\text{O}_2\text{C})_2\text{C}=\text{CHC}(\text{CH}_3)=\text{NO}_2\text{Na}$	Silica gel, CH_3OH	$(\text{C}_2\text{H}_5\text{O}_2\text{C})_2\text{C}=\text{CHCOCH}_3$ (23)	152
$n\text{-C}_6\text{H}_5\text{CH}(\text{NO}_2)\text{CO}_2\text{C}_6\text{H}_5\text{-}n$	CH_3OH , LiClO_4 , e^-	$n\text{-C}_6\text{H}_5\text{COCO}_2\text{C}_6\text{H}_5\text{-}n$ (76)	193
$\text{O}_2\text{N}(\text{CH}_2)_6\text{NO}_2$	ZnCl_2 , HCl , H_2O	$\text{OHC}(\text{CH}_2)_4\text{CHO}$ (—)	183
$\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{CH}_3$	1. NaOH 2. HCl	$\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{H}$ (55)	262
$\text{C}_2\text{H}_5\text{CH}(\text{NO}_2)(\text{CH}_2)_2\text{CO}_2\text{CH}_3$	$\text{KOC}_4\text{H}_9\text{-}t$, $t\text{-C}_4\text{H}_9\text{O}_2\text{H}$, $\text{Mo}(\text{CO})_6$ 1. NaOH 2. H^+	$\text{C}_2\text{H}_5\text{CO}(\text{CH}_2)_2\text{CO}_2\text{CH}_3$ (20) $\text{C}_2\text{H}_5\text{CO}(\text{CH}_2)_2\text{CO}_2\text{H}$ (65)	144 271
$\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{CH}_3$	$(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{Br}^-$, CH_3CN , O_2 , e^- 1. NaOH 2. HCl	$\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{CH}_3$ (76) $\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$ (53)	194 262
	$(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{Br}^-$, CH_3CN , O_2 , e^-	 (71)	194
$\text{CH}_3\text{CH}(\text{NO}_2)(\text{CH}_2)_2$	1. KOAc , CH_3OH , e^- 2. H_3O^+	$\text{CH}_3\text{CO}(\text{CH}_2)_2$ $\text{C}_2\text{H}_5\text{CO}(\text{CH}_2)_2\text{CHO}$ (75)	194
$\text{C}_2\text{H}_5\text{CH}(\text{NO}_2)(\text{CH}_2)_2\text{CH}$	1. NaOH 2. H_2SO_4	$\text{C}_2\text{H}_5\text{CO}(\text{CH}_2)_2\text{CO}_2\text{C}_2\text{H}_5$ (74)	272
$\text{C}_2\text{H}_5\text{CH}(\text{NO}_2)(\text{CH}_2)_2\text{CO}_2\text{C}_2\text{H}_5$	1. NaOH 2. H_2SO_4 3. Ac_2O , Py	 (84)	42
	1. NaOH 2. HCl , heat	CHO (93)	273
	1. $\text{Ba}(\text{OH})_2$ 2. H_2SO_4	 (66)	274
	1. NaOH 2. H_2SO_4	CHO (23-P)	275, 248
	1. OH^- 2. H^+ 1. NaOH 2. H_2SO_4	" (81-P)	276
	1. NaOH 2. H_2SO_4	CHO (58)	275, 248
	1. NaOH 2. H_2SO_4	" (20-25)	248

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
$ \begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	1. NaOH 2. H ₂ SO ₄	$ \begin{array}{c} \text{CHO} \quad (60) \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	277
$ \begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	1. NaOH 2. H ₂ SO ₄	$ \begin{array}{c} \text{CHO} \quad (80\text{-P}) \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	277
$ \begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	1. NaOH 2. H ₂ SO ₄	$ \begin{array}{c} \text{CHO} \quad (64) \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	278
$ \begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array} + \begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array} $	1. Ba(OH) ₂ 2. H ₂ SO ₄	$ \begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array} + \begin{array}{c} \text{CHO} \quad (62) \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array} $	279
$ \begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{CH}_2 \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	1. OH ⁻ 2. H ⁺	$ \begin{array}{c} \text{CHO} \quad (25) \\ \\ \text{CH}_2 \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	280
$ \begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H} \\ \\ \text{O} \end{array} $	H ₂ SO ₄	$ \begin{array}{c} \text{CHO} \quad (100) \\ \\ \text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H} \\ \\ \text{O} \end{array} $	281
$ \begin{array}{c} {}^{14}\text{CH}_2\text{NO}_2 \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	1. NaOH 2. H ₂ SO ₄	$ \begin{array}{c} {}^{14}\text{CHO} \quad (58) \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	282
$ \begin{array}{c} {}^{14}\text{CH}_2\text{NO}_2 \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	1. NaOH 2. H ₂ SO ₄	$ \begin{array}{c} {}^{14}\text{CHO} \quad (78\text{-P}) \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	282
$ \begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{H}-\text{C}-\text{NHAc} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	1. NaOH 2. HCl, heat	$ \begin{array}{c} \text{CHO} \quad (85) \\ \\ \text{H}-\text{C}-\text{NH}_2 \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	273

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.	
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{H}-\text{C}-\text{NHAc} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	1. NaOH 2. HCl, heat	$\begin{array}{c} \text{CHO} \quad (-) \\ \\ \text{H}-\text{C}-\text{NH}_2 \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	274	
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{AcNH}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	1. Ba(OH) ₂ 2. H ₂ SO ₄	$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{AcNH}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \quad (80) \\ \\ \text{AcNH}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	278
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{H}-\text{C}-\text{NHAc} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	"	$\begin{array}{c} \text{CHO} \quad (80) \\ \\ \text{H}-\text{C}-\text{NHAc} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	283 278	
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{H}-\text{C}-\text{NHAc} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} + \begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{AcNH}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	"	$\begin{array}{c} \text{CHO} \quad (84) \\ \\ \text{H}-\text{C}-\text{NHAc} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} + \begin{array}{c} \text{CHO} \quad (91) \\ \\ \text{AcNH}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	283 284, 285	
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{H}-\text{C}-\text{NHAc} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	"	$\begin{array}{c} \text{CHO} \quad (32) \\ \\ \text{H}-\text{C}-\text{NHAc} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	280, 286	
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{AcNH}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	"	$\begin{array}{c} \text{CHO} \quad (4) \\ \\ \text{AcNH}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	280, 286	
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{CH}_2 \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{AcO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{CH}_3 \end{array}$	1. NaOH 2. H ₂ SO ₄	$\begin{array}{c} \text{CHO} \quad (100) \\ \\ \text{CH}_2 \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$	279	
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{O} \diagup \text{CHC}_6\text{H}_5 \\ \quad \diagdown \quad \text{O} \\ \text{H}-\text{C}-\text{O} \end{array}$	1. NaOH 2. H ₂ SO ₄	$\begin{array}{c} \text{CHO} \quad (31-P) \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	41	
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{CH}_2\text{OH} \\ \\ \text{H}-\text{C}-\text{O} \diagup \text{CHC}_6\text{H}_5 \\ \quad \diagdown \quad \text{O} \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{NO}_2 \end{array}$	1. NaOH 2. H ₂ SO ₄ 3. Ba ₂ CO ₃	$\begin{array}{c} \text{CHO} \quad (52-B) \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{CH}_2\text{OH} \end{array}$	287	

724

725

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

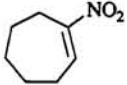
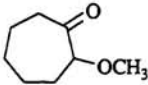
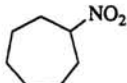
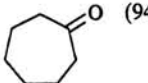

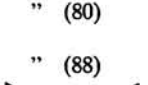
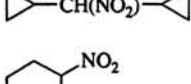
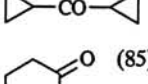
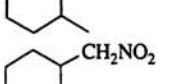
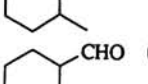
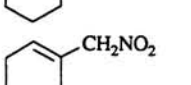
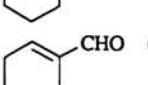
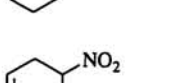
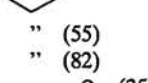
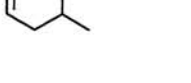
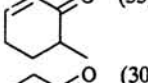

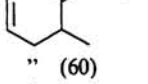
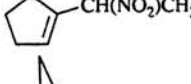
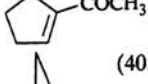
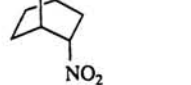
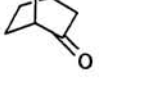






Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{CH}_2 \\ \\ \text{AcO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{CH}_2\text{OAc} \end{array}$	1. NaOH 2. H ₂ SO ₄	$\begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ (70)	288
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{CH}_2 \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{CH}_2\text{OAc} \end{array}$	1. Ba(OH) ₂ 2. H ₂ SO ₄	$\begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ (86)	289, 290
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{CH}_2 \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{CH}_2\text{OAc} \end{array}$	1. NaOH 2. H ₂ SO ₄	$\begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ (100)	284
$\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{AcO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{CH}_3 \end{array}$ + $\begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{AcO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{AcO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OAc} \\ \\ \text{CH}_3 \end{array}$	1. NH ₃ , CH ₃ OH 2. Ba(OH) ₂ 3. H ₂ SO ₄	$\begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{NHAc} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$ + $\begin{array}{c} \text{CHO} \\ \\ \text{AcNH}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$ (37)	279
C ₇ CH ₃ COCH ₂ C(CH ₃) ₂ CH ₂ NO ₂	1. (C ₂ H ₅) ₃ N 2. C ₁₆ H ₃₃ N(CH ₃) ₃ ⁺ MnO ₄ ⁻	CH ₃ COCH ₂ C(CH ₃) ₂ CHO (62)	261
	1. NaOCH ₃ , CH ₃ OH 2. TiCl ₃ , NH ₄ OAc, H ₂ O	 (70)	154
	1. NaOH 2. HCl	 (94-D)	10
	1. ZnCl ₂ , H ₂ O 2. K ₂ CO ₃	 (80)	179
	NaNO ₂ , <i>n</i> -C ₃ H ₇ ONO ₂ , DMSO	 (88)	197
	1. NaOH 2. HCl	 (96-D)	10
	1. LDA 2. MoO ₅ ·Py·HMPA	 (85)	145
	(C ₂ H ₅) ₃ N, CAN	 CHO (75)	148
	1. ZnCl ₂ , HCl 2. H ₂ O	 CHO (—)	183
	TiCl ₃ , H ₂ O	 (55)	162
	Silica gel, NaOCH ₃	 (82)	201
	TiCl ₃ , H ₂ O	 (35)	154
	TiCl ₃ , NH ₄ OAc, H ₂ O	 (30)	154
	NaOCH ₃ , TiCl ₃ , NH ₄ OAc, H ₂ O	 (60)	156
	1. KOC ₄ H ₉ - <i>t</i> 2. TiCl ₃	 COCH ₃ (80)	291
	1. NaOH 2. HCl	(40, 80-D)	292

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)


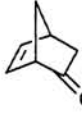
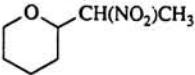
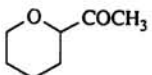
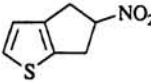
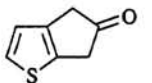
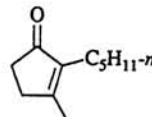
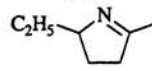




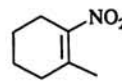
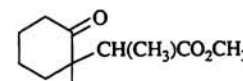
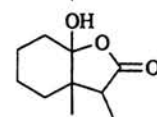
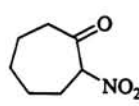
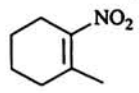
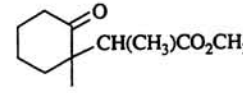
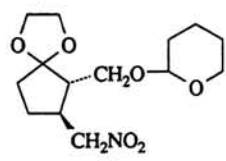
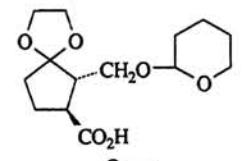
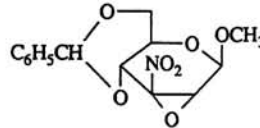
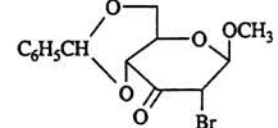
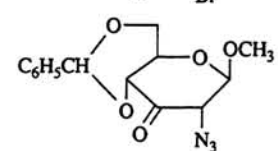
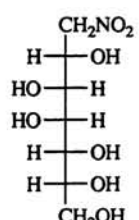
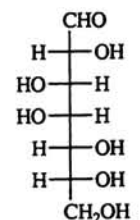
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. NaOCH ₃ , CH ₃ OH 2. TiCl ₃ , NH ₄ OAc	 (56)	92
	1. (CH ₃) ₂ NH 2. HCl	 (65)	293
	1. OH ⁻ 2. HCl	 (75)	81
C ₆ H ₅ CH ₂ NO ₂	1. KOH, MgSO ₄ 2. KMnO ₄	C ₆ H ₅ CHO (68, 97-D)	124
	1. KOH, CH ₃ OH 2. KMnO ₄ , MgSO ₄	" (83)	131
	1. NaOH, CH ₃ OH, Rose Bengal 2. O ₂ , hν	" (49)	140
	1. NaOCH ₃ , CH ₃ OH, -78° 2. O ₃ , DMS	" (68)	141
	TiCl ₃ , H ₂ O	" (80)	154
	1. (C ₂ H ₅) ₃ N 2. C ₁₆ H ₃₃ N(CH ₃) ₃ ⁺ MnO ₄ ⁻	" (89)	261
	1. (C ₂ H ₅) ₃ N 2. MoO ₃ ·Py·HMPA	C ₆ H ₅ CO ₂ H (75)	145
4-BrC ₆ H ₄ CH ₂ NO ₂	1. NaOC ₄ H ₉ -t 2. KMnO ₄	4-BrC ₆ H ₄ CHO (90)	127
<i>n</i> -C ₇ H ₁₅ NO ₂	1. H ₂ O ₂ 2. K ₂ CO ₃ , H ₂ O 3. HCl	<i>n</i> -C ₆ H ₁₃ CHO (78)	148
	1. (C ₂ H ₅) ₃ N 2. CAN	" (67)	148
	Silica gel, NaOCH ₃ 1. (C ₂ H ₅) ₃ N 2. C ₁₆ H ₃₃ N(CH ₃) ₃ ⁺ MnO ₄ ⁻	" (87) " (71)	200 261
	1. CH ₂ =CHCOCH ₃ , Al ₂ O ₃ 2. H ₂ O ₂ , K ₂ CO ₃ 3. NaOH, heat	 (60)	245
CH ₃ O ₂ C(CH ₂) ₆ NO ₂	1. CH ₂ =CHCOCH ₃ , Al ₂ O ₃ 2. H ₂ O ₂ , K ₂ CO ₃	CH ₃ O ₂ C(CH ₂) ₅ CO(CH ₂) ₂ COCH ₃ (50)	245
<i>n</i> -C ₃ H ₇ CH(NO ₂)C ₃ H ₇ - <i>n</i>	1. HCl, DMF 2. VCl ₂ , H ₂ O 3. NaOH	<i>n</i> -C ₃ H ₇ COC ₃ H ₇ - <i>n</i> (63)	170
C ₂ H ₅ CH(NO ₂)(CH ₂) ₂ COCH ₃	1. NaOH, CH ₃ OH 2. Rose Bengal, O ₂ , hν	C ₂ H ₅ CO(CH ₂) ₂ COCH ₃ (60)	140
	1. NaOCH ₃ , CH ₃ OH, -78° 2. O ₃ , DMS	" (83)	141
	1. KOC ₄ H ₉ -t 2. <i>t</i> -C ₄ H ₉ O ₂ H, Mo(CO) ₆	" (60)	144
	TiCl ₃ , H ₂ O	" (85)	153, 154
	NaOCH ₃ , TiCl ₃ , NH ₄ OAc, H ₂ O	" (90)	156
	Silica gel, NaOCH ₃	" (84)	200
	Silica gel, KMnO ₄	" (80)	202, 203
	TiCl ₃ , NH ₄ OAc, H ₂ O	 (20)	154
C ₂ H ₅ CO(CH ₂) ₂ CH(NO ₂)CH ₃	Silica gel, KMnO ₄	C ₂ H ₅ CO(CH ₂) ₂ COCH ₃ (73)	202, 203
CH ₃ COCH ₂ CH(CH ₃)CH(NO ₂)CH ₃	Silica gel, KMnO ₄	CH ₃ COCH ₂ CH(CH ₃)COCH ₃ (80)	202, 203
CH ₃ COCH ₂ C(CH ₃) ₂ CH ₂ NO ₂	1. (C ₂ H ₅) ₃ N 2. C ₁₆ H ₃₃ N(CH ₃) ₃ ⁺ MnO ₄ ⁻	CH ₃ COCH ₂ C(CH ₃) ₂ CHO (62)	261
<i>i</i> -C ₃ H ₇ CHOHCH(NO ₂)C ₂ H ₅	H ₂ SO ₄	<i>i</i> -C ₃ H ₇ CHOHCOC ₂ H ₅ I (40-50) + <i>i</i> -C ₃ H ₇ CH=C(NO ₂)C ₂ H ₅ II (10)	257
	1. OH ⁻ 2. HCl	I (40-50) + II (-)	256

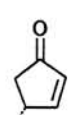
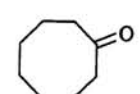
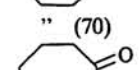
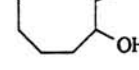
TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
$C_2H_5COCH=CHC(CH_3)=NO_2Na$	Silica gel, CH_3OH	$C_2H_5COCH=CHCOCH_3$ (38)	152
$O_2N(CH_3)_7NO_2$	1. $ZnCl_2$, HCl 2. H_2O	$OHC(CH_3)_5CHO$ (20-30)	183
$C_2H_5CH(NO_2)CH_2CH(NO_2)C_2H_5$	1. $(CH_3)_2NH$ 2. HCl	$C_2H_5COCH_2COC_2H_5$ (39)	293
$CH_3O_2C(CH_2)_6NO_2$	1. $NaOCH_3$, CH_3OH 2. H_2SO_4	$CH_3O_2C(CH_2)_5CHO$ (61)	294
	"	" (70)	295
$CH_3O_2C(CH_2)_2CH(NO_2)(CH_2)_2CO_2CH_3$	1. $NaOCH_3$, CH_3OH , -78° 2. O_3 , DMS	$CH_3O_2C(CH_2)_2CO(CH_2)_2CO_2CH_3$ (88)	141
	1. $NaOH$ 2. HCl	$HO_2C(CH_2)_2CO(CH_2)_2CO_2H$ (60)	263
	1. KOC_4H_9-t 2. $t-C_4H_9O_2H$, $VO(acac)_2$	 (82)	144
$C_2H_5CH(NO_2)(CH_2)_2$	$TiCl_3$, NH_4OAc , H_2O 1. $NaOCH_3$ 2. $TiCl_3$, NH_4OAc , H_2O $TiCl_3$, H_2O	" (70) " (70)	154 156
$n-C_3H_7CH(NO_2)(CH_2)_2CH$ 	"	$C_2H_5CO(CH_2)_2COCH_3$ (40)	154
$i-C_3H_7CH(NO_2)(CH_2)_2CH$ 	1. $KOAc$, CH_3OH , e^- 2. H_3O^+	$i-C_3H_7CO(CH_2)_2CHO$ (84)	195
	1. $CH_3CH=C(OTMS)OCH_3$, $TiCl_4$, $Ti(OC_2H_5)_4$ 2. H_2O , heat	 + (32)  (41)	165, 167
	H_2O_2 , K_2CO_3 , CH_3OH	$HO_2C(CH_2)_5CO_2H$ (90)	266a
	"	 (73)	168
	1. KOH 2. $KMnO_4$, $MgSO_4$	 (50)	296
	$LiBr$	 (75)	234
	LiN_3	 (83)	234
	1. $NaOH$ 2. H_2SO_4	 (70)	297

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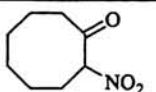
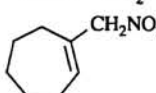
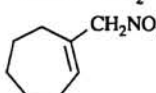
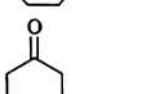
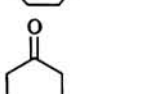
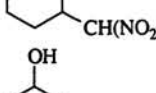
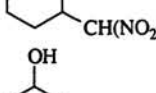
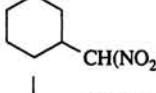
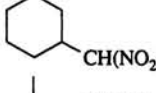
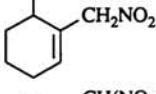
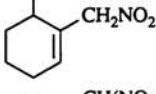
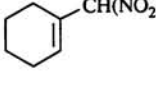
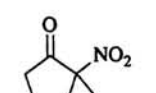


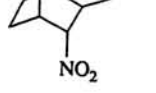

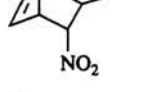

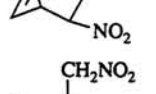
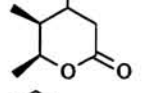
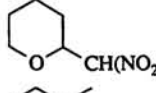
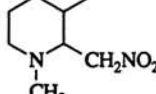
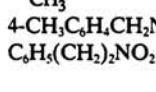



TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
$ \begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{HO}-\text{H} \\ \\ \text{HO}-\text{H} \\ \\ \text{HO}-\text{H} \\ \\ \text{H}-\text{OH} \\ \\ \text{H}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	1. NaOH 2. H ₂ SO ₄	$ \begin{array}{c} \text{CHO} \quad (80) \\ \\ \text{HO}-\text{H} \\ \\ \text{HO}-\text{H} \\ \\ \text{HO}-\text{H} \\ \\ \text{H}-\text{OH} \\ \\ \text{H}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	297
$ \begin{array}{c} \text{CH}_2\text{NO}_2 \\ \\ \text{H}-\text{OH} \\ \\ \text{H}-\text{NHAc} \\ \\ \text{H}-\text{OH} \\ \\ \text{HO}-\text{H} \\ \\ \text{H}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	1. Ba(OH) ₂ 2. H ₂ SO ₄	$ \begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHO} \quad (44) \\ \\ \text{H}-\text{OH} \\ \\ \text{H}-\text{NHAc} \\ \\ \text{H}-\text{OH} \\ \\ \text{HO}-\text{H} \\ \\ \text{H}-\text{OH} \end{array} $	298, 298a
$ \begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}_2\text{NO}_2 \\ \\ \text{HO}-\text{H} \\ \\ \text{H}-\text{NHAc} \\ \\ \text{H}-\text{OH} \\ \\ \text{HO}-\text{H} \\ \\ \text{H}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	"	$ \begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHO} \quad (56) \\ \\ \text{HO}-\text{H} \\ \\ \text{H}-\text{NHAc} \\ \\ \text{H}-\text{OH} \\ \\ \text{HO}-\text{H} \\ \\ \text{H}-\text{OH} \end{array} $	298, 298a
$ \begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}_2\text{NO}_2 \\ \\ \text{H}-\text{OH} \\ \\ \text{H}-\text{OH} \\ \\ \text{HO}-\text{H} \\ \\ \text{H}-\text{O}-\text{CHC}_6\text{H}_5 \\ \quad \\ \text{H}-\text{OH} \quad \text{O} \\ \\ \text{CH}_2-\text{O} \end{array} $	1. H ₂ SO ₄ 2. NaOH 3. H ₂ SO ₄	$ \begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHO} \quad (60\text{-B}) \\ \\ \text{H}-\text{OH} \\ \\ \text{H}-\text{OH} \\ \\ \text{HO}-\text{H} \\ \\ \text{H}-\text{OH} \\ \\ \text{H}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	299
$ \begin{array}{c} \text{OCH}_2\text{C}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2-\text{O}-\text{C}_6\text{H}_5 \\ \quad \\ \text{C}_6\text{H}_5\text{CH}_2\text{O} \quad \text{CH}_2\text{NO}_2 \\ \\ \text{CH}_2\text{OCH}_2\text{OCH}_3 \end{array} $	1. NaOCH ₃ , CH ₃ OH 2. O ₃	$ \begin{array}{c} \text{OCH}_2\text{C}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2-\text{O}-\text{C}_6\text{H}_5 \\ \quad \\ \text{C}_6\text{H}_5\text{CH}_2\text{O} \quad \text{CHO} \\ \\ \text{CH}_2\text{OCH}_2\text{OCH}_3 \end{array} $	(74) 300
$ \begin{array}{c} \text{OCH}_2\text{C}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2-\text{O}-\text{C}_6\text{H}_5 \\ \quad \\ \text{C}_6\text{H}_5\text{CH}_2\text{O} \quad \text{CH}_2\text{OCH}_2\text{OCH}_3 \\ \\ \text{CH}_2\text{NO}_2 \end{array} $	"	$ \begin{array}{c} \text{OCH}_2\text{C}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2-\text{O}-\text{C}_6\text{H}_5 \\ \quad \\ \text{C}_6\text{H}_5\text{CH}_2\text{O} \quad \text{CH}_2\text{OCH}_2\text{OCH}_3 \\ \\ \text{CHO} \end{array} $	(63) 300
$ \text{CH}_2=\text{C}(\text{NO}_2)(\text{CH}_2)_4\text{CO}_2\text{CH}_3 $	1. LiCH=CHCH(OTBDMS)C ₃ H _{11-n} , CuI, (n-C ₄ H ₉) ₃ P 2.  3. TiCl ₃ , NH ₄ OAc "	$ \begin{array}{c} \text{O} \\ \\ \text{C} \\ \\ \text{CH}_2\text{CO}(\text{CH}_2)_4\text{CO}_2\text{CH}_3 \\ \\ \text{CH}=\text{CHC}_3\text{H}_7 \\ \\ \text{OTBDMS} \end{array} $	(76) 160
$ \text{C}_8\text{H}_{15}\text{NO}_2 $	TiCl ₃ , H ₂ O	 (55)	154
	TiCl ₃ , NH ₄ OAc, H ₂ O 1. NaOH 2. TiCl ₃ , NH ₄ OAc, H ₂ O	 (70)  (90)	154 154

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TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	H ₂ O ₂ , K ₂ CO ₃ , CH ₃ OH	HO ₂ C(CH ₂) ₆ CO ₂ H (89)	266a
	TiCl ₃ , H ₂ O	 (57)	162
	1. NaOH 2. H ₂ SO ₄	 (65)	34
	1. NaOH 2. H ₂ SO ₄	 (80)	34
	1. NaOCH ₃ 2. TiCl ₃	 (92)	291
	1. NaOCH ₃ 2. TiCl ₃	 (81)	291
	NaOH, (NH ₄) ₂ S ₂ O ₈ H ₂ O ₂ , K ₂ CO ₃ , CH ₃ OH	" (61-66) HO ₂ CCH ₂ C(CH ₃) ₂ CH ₂ COCH ₃ (79)	150 266a
			
			
			
			
			
			
			
			
			
			
			
			
			
			
			

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TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

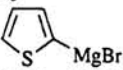

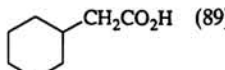
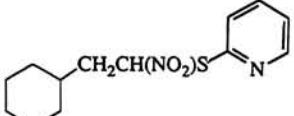
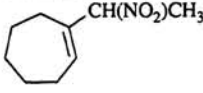
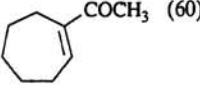
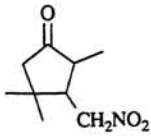
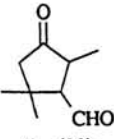
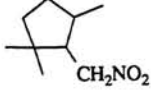
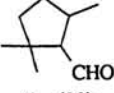
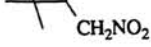
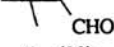
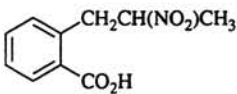
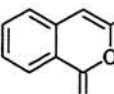
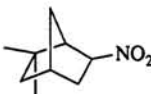
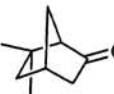
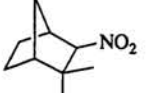
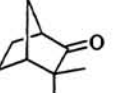


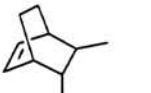
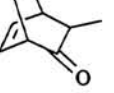
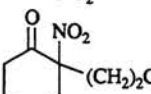
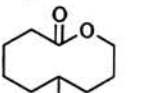
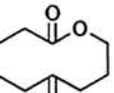
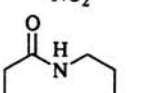
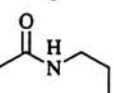
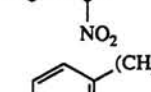
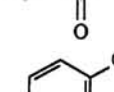
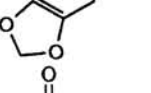
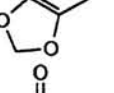
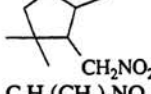
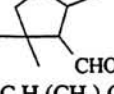



Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. NaOH, C ₂ H ₅ OH	" (64)	267
C ₆ H ₅ CH=C(NO ₂)CH ₃	2. H ₂ SO ₄ , H ₂ O, C ₅ H ₁₂	C ₆ H ₅ CH ₂ COCH ₃ (72)	228a
C ₆ H ₅ CH=CHNO ₂	1. (n-C ₄ H ₉) ₃ SnH		
	2. O ₃		
	1. 	(CH ₃ O) ₂ CHCH(C ₆ H ₅)  (84)	304
	2. H ₂ SO ₄ , CH ₃ OH		
	1. 2-CH ₃ OC ₆ H ₄ MgBr	C ₆ H ₅ CH(C ₆ H ₄ OCH ₃ -2)CH(OCH ₃) ₂ (76)	304
	2. H ₂ SO ₄ , CH ₃ OH		
	1. 3-ClC ₆ H ₄ MgBr	C ₆ H ₅ CH(C ₆ H ₄ Cl-3)CH(OCH ₃) ₂ (82)	304
	2. H ₂ SO ₄ , CH ₃ OH		
	1. 4-CF ₃ C ₆ H ₄ MgBr	C ₆ H ₅ CH(C ₆ H ₄ CF ₃ -4)CH(OCH ₃) ₂ (73)	304
	2. H ₂ SO ₄ , CH ₃ OH		
4-ClC ₆ H ₄ (CH ₂) ₂ NO ₂	1. NaOH, C ₂ H ₅ OH	4-ClC ₆ H ₄ CH ₂ CHO (36)	267
	2. H ₂ SO ₄ , H ₂ O, C ₅ H ₁₂		
C ₆ H ₅ CH(NO ₂)CH ₃	KNO ₂ , H ₂ SO ₄	C ₆ H ₅ COCH ₃ (—)	69
	1. NaOC ₄ H ₉ -t	" (90)	127
	2. KMnO ₄		
	NaOH, (NH ₄) ₂ S ₂ O ₈	" (72)	150
	NaNO ₂ , n-C ₃ H ₇ ONO, DMSO	" (79)	197
	1. (C ₂ H ₅) ₃ N	" (87)	261
	2. C ₁₆ H ₃₃ N(CH ₃) ₃ ⁺ MnO ₄ ⁻		
	TiCl ₃	 (89)	229
			
n-C ₈ H ₁₇ NO ₂	1. NaOCH ₃ , CH ₃ OH	n-C ₇ H ₁₅ CH(OCH ₃) ₂ (—)	33
	2. H ₂ SO ₄		
	1. NaOC ₄ H ₉ -t	n-C ₇ H ₁₅ CHO (85)	127
	2. KMnO ₄		
	1. KOH, CH ₃ OH	" (83)	131
	2. KMnO ₄ , MgSO ₄		
	NaOH, 8-azafavin (28)	" (—)	139
	1. NaOH, CH ₃ OH, Rose Bengal	" (67)	140
	2. O ₂ , hν		
	1. NaOCH ₃ , CH ₃ OH, -78°	" (65)	141
	2. O ₃ , DMS		
	1. KOC ₄ H ₉ -t	" (45)	144
	2. t-C ₄ H ₉ O ₂ H, VO(acac) ₂		
	1. HCl, DMF	" (24)	170
	2. VCl ₂ , H ₂ O, NaOH		
	CrCl ₂ , CH ₃ OH, HCl	" (53-D)	172
	NaNO ₂ , n-C ₃ H ₇ ONO, DMF, H ⁺	n-C ₇ H ₁₅ CO ₂ H (9-52)	196
	HCl, reflux	n-C ₆ H ₁₃ COCH ₃ (65)	50
n-C ₆ H ₁₃ CH(NO ₂)CH ₃	1. HCl, DMF	" (71)	170
	2. VCl ₂ , H ₂ O		
	3. NaOH		
	CrCl ₂ , CH ₃ OH, HCl	" (61-D)	172
	NaNO ₂ , n-C ₃ H ₇ ONO, DMF	" (47-83)	196
	NaNO ₂ , n-C ₃ H ₇ ONO, DMSO	" (83)	197
CH ₂ =C(NO ₂)C ₆ H _{13-n}	1. (i-C ₄ H ₉) ₃ Al	i-C ₅ H ₁₁ COC ₆ H _{13-n} I (50) +	259
	2. (C ₂ H ₅) ₂ O	i-C ₅ H ₁₁ CH(NO ₂)C ₆ H _{13-n} II (38)	
	3. HCl, rt		
	1. (i-C ₄ H ₉) ₃ Al	I (86) + II (7)	259
	2. H ₃ O ⁺		
CH ₃ CO(CH ₂) ₂ CH(NO ₂)C ₃ H _{7-n}	NaNO ₂ , n-C ₃ H ₇ ONO, DMSO	CH ₃ CO(CH ₂) ₂ COC ₃ H _{7-n} (71)	197
CH ₃ COCH ₂ CH(CH ₃)CH(NO ₂)C ₂ H ₅	Silica gel, KMnO ₄	CH ₃ COCH ₂ CH(CH ₃)COC ₂ H ₅ (78)	202, 203
CH ₃ COCH ₂ C(CH ₃) ₂ CH(NO ₂)CH ₃	1. NaOH, C ₂ H ₅ OH	CH ₃ COCH ₂ C(CH ₃) ₂ COCH ₃ (70)	305
	2. HCl		
CH ₃ C(CH ₃)=CHCO(CH ₂) ₂ NO ₂	1. NaOH	CH ₃ C(CH ₃)=CHCO(CH ₂) ₂ CHO (—)	129
	2. KMnO ₄		
i-C ₄ H ₉ CO(CH ₂) ₂ NO ₂	1. NaOH	i-C ₄ H ₉ CO(CH ₂) ₂ CHO (—)	129
	2. KMnO ₄		
i-C ₃ H ₇ COCH=CHC(CH ₃)=NO ₂ Na	Silica gel, CH ₃ OH	i-C ₃ H ₇ COCH=CHCOCH ₃ (41)	152
C ₂ H ₅ COC(CH ₃)=CHC(CH ₃)=NO ₂ Na	Silica gel, CH ₃ OH	C ₂ H ₅ COC(CH ₃)CHCOCH ₃ (56)	152

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
$O_2N(CH_2)_8NO_2$	1. $ZnCl_2$, HCl 2. H_2O	$OHC(CH_2)_6CHO$ (—)	183
$n-C_4H_9SO_2(CH_2)_2CH(NO_2)CH_3$	1. NaOH 2. H_2SO_4	$n-C_4H_9SO_2(CH_2)_2COCH_3$ (—)	306
CH_3OCH_2 	1. NaOCH ₃ , CH ₃ OH 2. $TiCl_3$, NH_4OAc	(60)	92
 $(CH_2)_2CH(NO_2)C_3H_7-i$	1. NaOH, CH_3OH , -78° 2. O_3 , DMS	(74)	142
$CH_3CO(CH_2)_2CH(NO_2)(CH_2)_2CO_2C_2H_5$	C_2H_5OH , NaO_2CH , e^-	$CH_3CO(CH_2)_2CO(CH_2)_2CO_2C_2H_5$ (88)	193
$CH_3CH(OCH_2CH=CH_2)CH(NO_2)C_2H_5$	1. DBU, $TMSCl$ 2. MCPBA	$CH_3CH(OCH_2CH=CH_2)COC_2H_5$ (81)	143b
$n-C_5H_{11}CH(OAc)CH(NO_2)CH_3$	CH_3OH , $NaOAc$, e^-	$n-C_5H_{11}CH(OAc)COCH_3$ (40–43)	193
$i-C_4H_9CH(NO_2)(CH_2)_2CH$ 	1. KOAc, CH_3OH , e^- 2. H_3O^+	$i-C_4H_9CO(CH_2)_2CHO$ (85)	195
$n-C_4H_9CH(NO_2)(CH_2)_2CH$ 	"	$n-C_4H_9CO(CH_2)_2CHO$ (82)	195
$CH_3O_2CCH(CH_3)CH_2CH(NO_2)(CH_2)_2CO_2-$ CH_3	1. NaOH 2. HCl	$HO_2CCH(CH_3)CH_2CO(CH_2)_2CO_2H$ (52)	262
$CH_3O_2CCH_2CH(CH_3)CH(NO_2)(CH_2)_2CO_2-$ CH_3	1. NaOH 2. HCl	$HO_2CCH_2CH(CH_3)CO(CH_2)_2CO_2H$ (63)	262
$CH_3CO(CH_2)_2CH(NO_2)(CH_2)_2CH$ 	1. OH^- 2. H^+	$CH_3CO(CH_2)_2CO(CH_2)_2CH$ (50)	307
$(C_2H_5O)_2CH$ 	1. KOC_4H_9-t 2. $t-C_4H_9O_2H$, $VO(acac)_2$	(62)	144
$t-C_4H_9O_2CC(CH_3)_2C(CH_3)_2CH_2NO_2$	1. $NaOC_4H_9-t$ 2. $KMnO_4$	$t-C_4H_9O_2CC(CH_3)_2C(CH_3)_2CHO$ (91)	126, 127
$CH_3CH(OAc)(CH_2)_2CH(NO_2)(CH_2)_2-$ $CO_2C_2H_5$	C_2H_5OH , $NaOAc$, e^-	$CH_3CH(OAc)(CH_2)_2CO(CH_2)_2CO_2C_2H_5$ (55–62)	193
	1. NaOCH ₃ , CH_3OH 2. $TiCl_3$, NH_4OAc 3. H_3O^+ 4. Ac_2O	(20)	308
$(CH_3O)_2P(O)CH(C_6H_5)CH_2NO_2$	1. NaOCH ₃ 2. O_3 , DMS	$(CH_3O)_2P(O)CH(C_6H_5)CHO$ (30)	252
$(C_6H_5)_2P(O)CH(C_6H_5)CH_2NO_2$	1. NaOCH ₃ , CH_3OH 2. O_3 , DMS	$(C_6H_5)_2P(O)CH(C_6H_5)CHO$ (67)	255
	1. NaOCH ₃ , CH_3OH 2. Rose Bengal, O_2 , $h\nu$	" (87)	256
	1. NaOH 2. H_2SO_4	(84-P)	309
C_9 	1. NaOCH ₃ 2. $TiCl_3$	(66)	291

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. NaOCH ₃ 2. TiCl ₃	 (60)	291
	1. NaOH 2. KMnO ₄	 (64)	310
	1. NaOH 2. O ₃ , CH ₃ OH	 (90)	310
	1. NaOCH ₃ , CH ₃ OH 2. TiCl ₃ , NH ₄ OAc 3. H ₃ O ⁺ 4. Ac ₂ O	 (52)	308
	1. NaOH 2. H ₂ SO ₄ , CH ₃ OH 3. Ac ₂ O	 (84)	308
	1. OH ⁻ 2. KMnO ₄	 (—)	119
	1. OH ⁻ 2. KMnO ₄	 (—)	311
	1. NaOH, CH ₃ OH 2. H ₂ SO ₄	 (55)	301
	"	 (—)	301
	1. NaOH 2. H ⁺	HO ₂ C(CH ₂) ₄ CO(CH ₂) ₂ CO ₂ H (73)	99
	1. (C ₂ H ₅) ₃ N 2. CAN, heat	 (76)	98
	1. LiOCH ₃ , Na ₂ B ₄ O ₇ 2. KMnO ₄	 (68)	136
	1. NaOH, C ₂ H ₅ OH 2. H ₂ SO ₄ , H ₂ O, C ₃ H ₁₂	 (29)	267
	"	 (53)	312
	1. NaOCH ₃ , CH ₃ OH 2. H ₂ SO ₄	 (—)	33
	1. NaOC ₂ H ₅ 2. KMnO ₄	C ₆ H ₅ (CH ₂) ₂ CHO (82)	127
	1. ZnCl ₂ , HCl 2. HCl, H ₂ O	 (60)	182

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TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)


Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
$C_6H_5CH(NO_2)C_2H_5$	$SnCl_2, HCl$	$C_6H_5COC_2H_5$ (—)	69
$C_6H_5CH_2CH(NO_2)CH_3$	1. HCl, DMF 2. VCl_2, H_2O 3. $NaOH$	$C_6H_5CH_2COCH_3$ (65)	170
	1. $DBU, TMSCl$ 2. $MCPBA$	" (92)	143b
	1. $NaOH, C_2H_5OH$ 2. H_2SO_4, H_2O, C_3H_{12}	" (89)	267
$C_6H_5CH=C(NO_2)CH_3$	1. $(n-C_4H_9)_3SnH$ 2. O_3	" (97)	228a
$4-CH_3OC_6H_4CH=CHNO_2$	"	$4-CH_3OC_6H_4CH_2CHO$ (70)	228a
$4-ClC_6H_4CH_2CH(NO_2)CH_3$	1. $DBU, TMSCl$ 2. $MCPBA$	$4-ClC_6H_4CH_2COCH_3$ (98)	143b
$4-CH_3C_6H_4(CH_2)_2NO_2$	1. $NaOH, C_2H_5OH$ 2. H_2SO_4, H_2O, C_3H_{12}	$4-CH_3C_6H_4CH_2CHO$ (65)	267
$4-CH_3OC_6H_4(CH_2)_2NO_2$	"	$4-CH_3OC_6H_4CH_2CHO$ (67)	267
$i-C_4H_9CO(CH_2)_2CH(NO_2)CH_3$	1. $NaOH$ 2. $KMnO_4$	$i-C_4H_9CO(CH_2)_2COCH_3$ (—)	129
$C_2H_5C(CH_3)=CHCO(CH_2)_2NO_2$	1. $NaOH$ 2. $KMnO_4$	$C_2H_5C(CH_3)=CHCO(CH_2)_2CHO$ (—)	129
$C_2H_5CH(CH_3)CH_2CO(CH_2)_2NO_2$	1. $NaOH$ 2. $KMnO_4$	$C_2H_5CH(CH_3)CH_2CO(CH_2)_2CHO$ (—)	129
$C_6H_5CH=CHCH_2NO_2$	$(C_2H_5)_3N, CAN$	$C_6H_5CH=CHCHO$ (78)	148
$CH_3CH(NO_2)CH=CHCOCH=CH-CH(NO_2)CH_3$	1. KOH 2. $(CH_3O)_2SO_2, heat$	$CH_3COCH=CHCOCH=CHCOCH_3$ (50)	151
$CH_3C(CH_3)=CHCO(CH_2)_2CH(NO_2)CH_3$	1. $NaOH$ 2. $KMnO_4$	$CH_3C(CH_3)=CHCO(CH_2)_2COCH_3$ (—)	129
	Silica gel, CH_3OH	(51)	152
$C_2H_5CH(NO_2)C(CH_3)_2CH_2COCH_3$	CH_3OH, NaO_2CH, e^-	$C_2H_5COC(CH_3)_2CH_2COCH_3$ (60)	193
$n-C_4H_9SO_2(CH_2)_2CH(NO_2)C_2H_5$	1. $NaOH$ 2. H_2SO_4	$n-C_4H_9SO_2(CH_2)_2COC_2H_5$ (—)	306
$C_2H_5CH(NO_2)C(CH_3)_2CH_2COCH_3$	1. $NaOH, C_2H_5OH$ 2. HCl	$C_2H_5COC(CH_3)_2CH_2COCH_3$ (70)	305
$n-C_3H_7CH=C(CH_3)CH_2NO_2$	1. $NaOCH_3$ 2. $TiCl_3$	$n-C_3H_7CH=C(CH_3)CHO$ (50)	291
$(CH_3)_2C=CHCO(CH_2)_2CH(NO_2)CH_3$	1. $NaOH$ 2. $KMnO_4$	$CH_3C(CH_3)=CHCO(CH_2)_2COCH_3$ (—)	129
$2-HOC_6H_4CH=C(NO_2)CH_3$	$NaH_2PO_2, RaNi, H^+$	$2-HOC_6H_4CH_2COCH_3$ (70)	226
$4-HOC_6H_4CH=C(NO_2)CH_3$	"	$4-HOC_6H_4CH_2COCH_3$ (56)	226
$4-CH_3OC_6H_4CH=CHNO_2$	"	$4-CH_3OC_6H_4CH_2CHO$ (53)	226
$4-ClC_6H_4CH=C(NO_2)CH_3$	1. $CH_2=CHCH_2TMS, AlCl_3$ 2. $NaOCH_3, CH_3OH$ 3. $TiCl_3, NH_4OAc$	$4-ClC_6H_4CH(CH_2CH=CH_2)COCH_3$ (55)	157
$4-BrC_6H_4CH=CH(NO_2)CH_3$	1. $LiHB(C_4H_9-s)_3$ 2. H_2SO_4	$4-BrC_6H_4CH_2COCH_3$ (82)	224
	$NaH_2PO_2, RaNi, H^+$	" (77)	226
$C_6H_5CH=C(NO_2)CH_3$	1. $CH_3OH, SnCl_2$ 2. H^+	$C_6H_5CH(OCH_3)COCH_3$ (93)	221
	1. $LiHB(C_4H_9-s)_3$ 2. H_2SO_4	$C_6H_5CH_2COCH_3$ (80)	224
	1. $LiAlH_4$ 2. H^+	" (75)	225
	$NaH_2PO_2, RaNi, H^+$	" (88)	226
	1. $C_2H_5OH, SnCl_2$ 2. H^+	$C_6H_5CH(OC_2H_5)COCH_3$ (95)	221
	1. $C_2H_5SH, SnCl_2$ 2. H^+	$C_6H_5CH(SC_2H_5)COCH_3$ (90)	221
	1. $CH_2=CHCH_2TMS, AlCl_3$ 2. $NaOCH_3, CH_3OH$ 3. $TiCl_3, NH_4OAc$	$C_6H_5CH(CH_2CH=CH_2)COCH_3$ (51)	157
	1. $C_6H_5CH_2OH, SnCl_2$ 2. H^+	$C_6H_5CH(OCH_2C_6H_5)COCH_3$ (88)	221
	1. $NaCH(CO_2C_2H_5)_2$ 2. H^+	$C_6H_5CH(COCH_3)CH(CO_2C_2H_5)_2$ (27)	36

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

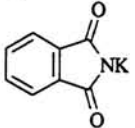
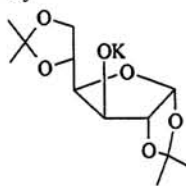
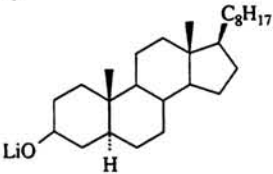
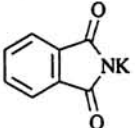

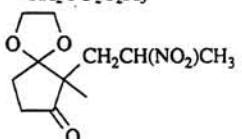
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
$\text{CH}_3\text{CH}=\text{C}(\text{NO}_2)\text{SC}_6\text{H}_5$	1. NaOCH_3 2. O_3	$\text{CH}_3\text{OCH}(\text{CH}_3)\text{COSC}_6\text{H}_5$ (79)	313
	1. 	(68)	143a
	2. O_3	$\text{CH}_3\text{CHOHCOSC}_6\text{H}_5$ (58)	313
	1. KOH 2. O_3	$\text{TsCH}(\text{CH}_3)\text{COSC}_6\text{H}_5$ (56)	313
	1. NaTs 2. O_3	$\text{FCH}_2\text{CONHCH}(\text{CH}_3)\text{COSC}_6\text{H}_5$ (62)	313
	1. FCH_2CONHK 2. O_3	$i\text{-C}_3\text{H}_7\text{OCH}(\text{CH}_3)\text{COSC}_6\text{H}_5$ (61)	313
	1. $\text{NaOC}_3\text{H}_7\text{-}i$ 2. O_3	$(\text{CH}_3\text{O}_2\text{C})_2\text{CHCH}(\text{CH}_3)\text{COSC}_6\text{H}_5$ (60)	313
	1. $\text{C}_6\text{H}_5\text{Li}$ 2. O_3	$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{COSC}_6\text{H}_5$ (39)	313
	1. $\text{C}_6\text{H}_5\text{COCH}_2\text{Li}$ 2. O_3	$\text{C}_6\text{H}_5\text{COCH}_2\text{CH}(\text{CH}_3)\text{COSC}_6\text{H}_5$ (43)	313
	1. 	$\text{OCH}(\text{CH}_3)\text{COSC}_6\text{H}_5$ (51)	313
	2. O_3		
	1. 	$\text{C}_6\text{H}_5\text{SCOCH}(\text{CH}_3)\text{O}$ (55)	313
	2. O_3		
	1. $\text{C}_6\text{H}_5\text{CH}_2\text{NTsLi}$ 2. O_3	$\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{Ts})\text{CH}(\text{CH}_3)\text{COSC}_6\text{H}_5$ (67)	313
	1. 	(68)	313
	2. O_3		
	1. NaTs 2. O_3	$\text{TsCH}(\text{CH}_3)\text{COSC}_6\text{H}_5$ (56)	313
	1. KOAc , CH_3OH , e^- 2. H_3O^+	$n\text{-C}_3\text{H}_7\text{CO}(\text{CH}_2)_2\text{CHO}$ (89)	195
$i\text{-C}_3\text{H}_7\text{CH}(\text{NO}_2)(\text{CH}_2)_2\text{CH}$ 	1. NaOH 2. HCl	$\text{HO}_2\text{CCH}(\text{CH}_3)\text{CH}_2\text{COCH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$ (84)	263
$\text{CH}_3\text{O}_2\text{CCH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{NO}_2)\text{CH}_2\text{-CH}(\text{CH}_3)\text{CO}_2\text{CH}_3$	1. NaOH 2. HCl	$\text{HO}_2\text{CCH}(\text{CH}_3)\text{CH}_2\text{COCH}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{H}$ (45)	263
$\text{CH}_3\text{O}_2\text{CCH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{NO}_2)\text{CH}(\text{CH}_3)\text{-CH}_2\text{CO}_2\text{C}_2\text{H}_5$	1. NaOH 2. HCl	$\text{HO}_2\text{CCH}_2\text{CH}(\text{CH}_3)\text{COCH}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{H}$ (12)	263
	NaOH , H_2O , $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{Br}^-$	(—)	314

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. NaOCH ₃ 2. TiCl ₃ , NH ₄ OAc	(77)	296
	1. NaOCH ₃ 2. O ₃ TiCl ₃ , NH ₄ OAc, H ₂ O	" (63)	296
	1. NaOCH ₃ , CH ₃ OH 2. TiCl ₃ , NH ₄ OAc	(70)	154
	1. NaOCH ₃ , CH ₃ OH 2. TiCl ₃ , NH ₄ OAc	CH ₃ O ₂ C(CH ₂) ₄ CO(CH ₂) ₂ CH(OCH ₃) ₂ (79)	315
	1. LiOCH ₃ 2. NaMnO ₄	(70)	128
	1. KOH, CH ₃ OH 2. KMnO ₄ , MgSO ₄	(85)	131
	1. KOH, CH ₃ OH 2. KMnO ₄ , MgSO ₄	(95)	131
C ₁₀ 	1. NaOCH ₃ 2. TiCl ₃	(40)	291
	1. KOH 2. H ₂ O	(12)	120
	1. OH ⁻ 2. KMnO ₄	(61)	117, 122
	1. OH ⁻ 2. KMnO ₄	(-)	117
	1. OH ⁻ 2. KMnO ₄	(-)	122
	1. OH ⁻ 2. KMnO ₄	(-)	118
	1. OH ⁻ 2. KMnO ₄	(-)	119
	1. KOH 2. H ₂ SO ₄	(48)	316

746

 C₁₀

747

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. $(C_2H_5)_3N$ 2. $C_{16}H_{33}N(CH_3)_7^- MnO_4^-$	" (65)	261
	1. $NaOCH_3, CH_3OH$ 2. $TiCl_3, NH_4OAc$ 3. H_3O^+ 4. Ac_2O, H^+		(43) 308
	1. $NaOH$ 2. H_2SO_4, CH_3OH 3. Ac_2O, H^+ 1. OH^- 2. $KMnO_4$	" (85)	308
			(52) 121
	$C_6H_6, h\nu$		(14) 244
		+	(33)
		+	(49)
	H_2O_2, K_2CO_3, CH_3OH		(88) 266a
	H_2O_2, K_2CO_3, CH_3OH	$HO_2C(CH_2)_4CO(CH_2)_2COCH_3$ (61)	266a
	1. $LiHB(C_4H_9-s)_3$ 2. H_2SO_4		(-) 317
	1. $(C_2H_5)_3N$ 2. $CAN, heat$		(76) 98
	1. $NaOCH_3$ 2. $TiCl_3, NH_4OAc$		(80) 99
	1. $LiOCH_3$ 2. $KMnO_4$	" (95)	99
	1. $NaH, t-C_4H_9OH$ 2. $KMnO_4$ 3. H_2SO_4		(60) 102

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

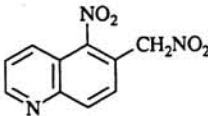
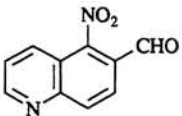
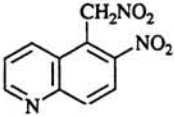
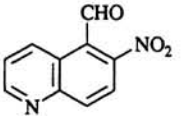
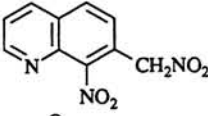
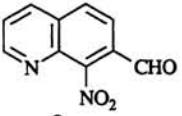
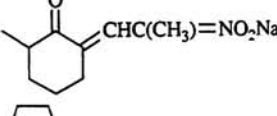
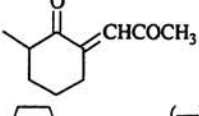
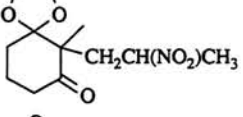
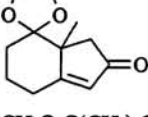
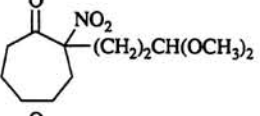
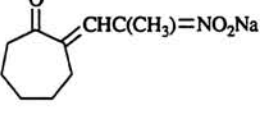
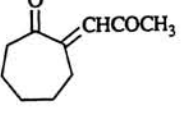
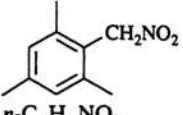
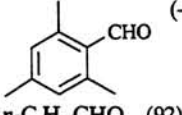
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. KOH 2. KMnO ₄ , Na ₂ B ₂ O ₇	 (92)	132, 318
	"	 (88)	132, 318
	"	 (85)	132, 318
	Silica gel, CH ₃ OH	 (34)	152
	NaOH, H ₂ O, (n-C ₄ H ₉) ₄ N ⁺ Br ⁻	 (—)	314
	1. NaOCH ₃ , CH ₃ OH 2. TiCl ₃ , NaOAc	CH ₃ O ₂ C(CH ₂) ₂ CO(CH ₂) ₂ CH(OCH ₃) ₂ (87)	315
	Silica gel, CH ₃ OH	 (54)	152
	1. ZnCl ₂ , H ₂ O 2. K ₂ CO ₃	 (—)	180
<i>n</i> -C ₁₀ H ₂₁ NO ₂	1. NaOC ₂ H ₅ - <i>t</i> 2. KMnO ₄	<i>n</i> -C ₉ H ₁₉ CHO (92)	127
C ₆ H ₅ (CH ₂) ₄ NO ₂	1. ZnCl ₂ , H ₂ O 2. CH ₃ OH, H ⁺	C ₆ H ₅ (CH ₂) ₃ CH(OCH ₃) ₂ (—)	182
CH ₃ C(CH ₃)=CHCO(CH ₂) ₂ CH(NO ₂)C ₂ H ₅	1. NaOH 2. KMnO ₄	CH ₃ C(CH ₃)=CHCO(CH ₂) ₂ COC ₂ H ₅ (—)	129
C ₂ H ₅ C(CH ₃)=CHCO(CH ₂) ₂ CH(NO ₂)CH ₃	1. NaOH 2. KMnO ₄	C ₂ H ₅ C(CH ₃)=CHCO(CH ₂) ₂ COCH ₃ (—)	129
<i>i</i> -C ₄ H ₉ CO(CH ₂) ₂ CH(NO ₂)C ₂ H ₅	1. NaOH 2. KMnO ₄	<i>i</i> -C ₄ H ₉ CO(CH ₂) ₂ COC ₂ H ₅ (—)	129
<i>s</i> -C ₄ H ₉ CH ₂ CO(CH ₂) ₂ CH(NO ₂)CH ₃	1. NaOH 2. KMnO ₄	<i>s</i> -C ₄ H ₉ CH ₂ CO(CH ₂) ₂ COCH ₃ (—)	129
CH ₂ =CH(CH ₂) ₃ CH=CHCH ₂ CH(NO ₂)CH ₃	1. TiCl ₃ , NH ₄ OAc, H ₂ O 2. HO(CH ₂) ₂ OH CH ₃ OH, NaO ₂ CH, e ⁻	CH ₂ =CH(CH ₂) ₃ CH=CHCH ₂ COCH ₃ (70)	158
<i>n</i> -C ₆ H ₁₃ CH(NO ₂)(CH ₂) ₂ CN	NaHPO ₂ , RaNi, H ⁺	<i>n</i> -C ₆ H ₁₃ CO(CH ₂) ₂ CN (88)	193
4-CH ₃ OC ₆ H ₄ CH=C(NO ₂)CH ₃	1. (n-C ₄ H ₉) ₃ SnH 2. O ₃	4-CH ₃ OC ₆ H ₄ CH ₂ COCH ₃ (92) " (95)	226 228a
4-CH ₃ C ₆ H ₄ CH=C(NO ₂)CH ₃	1. (n-C ₄ H ₉) ₃ SnH 2. MCPBA	4-CH ₃ C ₆ H ₄ CH ₂ COCH ₃ (99)	228a
4-NCC ₆ H ₄ CH=C(NO ₂)CH ₃	"	4-NCC ₆ H ₄ CH ₂ COCH ₃ (95)	228a
CH ₃ CH=C(C ₆ H ₅)CH ₂ NO ₂	1. NaOCH ₃ 2. TiCl ₃	CH ₃ CH=C(C ₆ H ₅)CHO (51)	291
C ₂ H ₅ CH=CH(CH ₂) ₂ CO(CH ₂) ₃ NO ₂	1. NaOH 2. H ₂ SO ₄	C ₂ H ₅ CH=CH(CH ₂) ₂ CO(CH ₂) ₂ CHO (45)	319
C ₆ H ₅ CH ₂ CH(NO ₂)CH ₂ CO ₂ C ₂ H ₅	1. NaOH 2. HCl	C ₆ H ₅ CH ₂ COCH ₂ CO ₂ H (91)	263
C ₆ H ₅ CH=C(NO ₂)C ₂ H ₅	1. CH ₂ =CHCH ₂ TMS, AlCl ₃ 2. NaOCH ₃ , CH ₃ OH 3. TiCl ₃ , NH ₄ OAc	C ₆ H ₅ CH(CH ₂ CH=CH ₂)COC ₂ H ₅ (62)	157

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

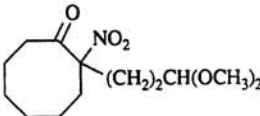
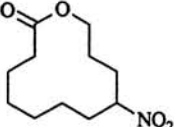
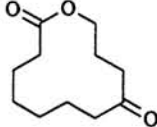
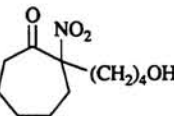
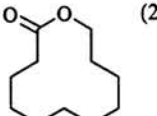
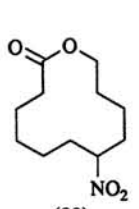

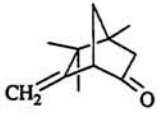
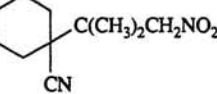
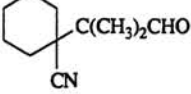
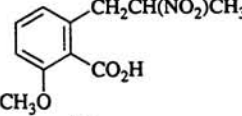
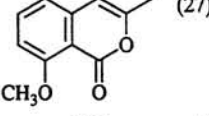
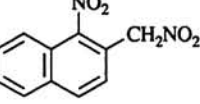
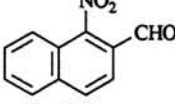
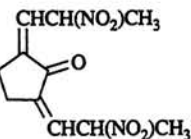
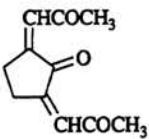
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
$C_6H_5CH_2CH(NO_2)C_2H_5$	1. NaOH, C_2H_5OH 2. H_2SO_4 , H_2O , C_5H_{12}	$C_6H_5CH_2COC_2H_5$ (91)	267
$4-CH_3C_6H_4CH_2CH(NO_2)CH_3$	1. DBU, TMSCl 2. MCPBA	$4-CH_3C_6H_4CH_2COCH_3$ (99)	143b
$4-CH_3OC_6H_4CH_2CH(NO_2)CH_3$	"	$4-CH_3OC_6H_4CH_2COCH_3$ (97)	143b
$4-NCC_6H_4CH_2CH(NO_2)CH_3$	"	$4-NCC_6H_4CH_2COCH_3$ (95)	143b
$C_6H_5CH(OCH_3)CH(NO_2)CH_3$	"	$C_6H_5CH(OCH_3)COCH_3$ (95)	143b
$3-O_2NC_6H_4CH(OCH_3)CH(NO_2)CH_3$	"	$3-O_2NC_6H_4CH(OCH_3)COCH_3$ (73)	143b
$3,4-(CH_3O)_2C_6H_3(CH_2)_2NO_2$	1. NaOH, C_2H_5OH 2. H_2SO_4 , H_2O , C_5H_{12} "	$3,4-(CH_3O)_2C_6H_3CH_2CHO$ (66)	267
$4-ClC_6H_4CH=C(NO_2)C_2H_5$	$NaOCH_3$, CH_3OH ; $TiCl_3$, NH_4OAc	" (59)	157
	$CH_2=CHCH_2TMS$, $TiCl_3$, $CH_3O(CH_2)_2OCH_3$	$4-ClC_6H_4CH(CH_2CH=CH_2)COC_2H_5$ (55)	157
	"	" (49)	157
$4-CH_3OC_6H_4CH=C(NO_2)CH_3$	1. $CH_2=CHCH_2TMS$, $AlCl_3$ 2. $NaOCH_3$, CH_3OH 3. $TiCl_3$, NH_4OAc	$4-CH_3OC_6H_4CH(CH_2CH=CH_2)COCH_3$ (48)	157
	1. $CH_2=CHCH_2TMS$, $AlCl_3$ 2. $TiCl_3$, $CH_3O(CH_2)_2OCH_3$	" (59)	157
C_{11}			
	1. $NaOCH_3$, CH_3OH 2. $TiCl_3$, $NaOAc$	$CH_3O_2C(CH_2)_6CO(CH_2)_2CH(OCH_3)_2$ (83)	315
	1. $(C_2H_5)_3N$ 2. CAN, heat	 (81)	98
	1. $NaOCH_3$ 2. $TiCl_3$, NH_4OAc	" (88)	99
	1. KH, heat 2. dil HCl	 (21)	102
		+  (5)	
	1. OH^- 2. $KMnO_4$	 (88)	123
	1. $NaOC_4H_9-t$ 2. $KMnO_4$	 (81)	126, 127
	1. $NaOCH_3$, CH_3OH 2. $TiCl_3$, NH_4OAc 3. H_3O^+ 4. Ac_2O , H^+	 (27)	308
	1. OH^- 2. $KMnO_4$, borate buffer	 (82)	132
		" (82)	318
	1. KOH 2. $KMnO_4$, $Na_2B_4O_7$ 1. KOH 2. $(CH_3O)_2SO_2$, heat	 (55)	151

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

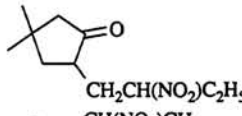
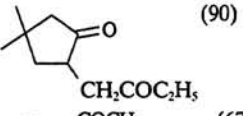
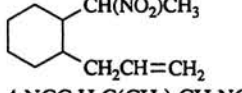
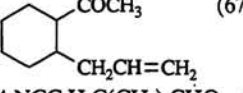
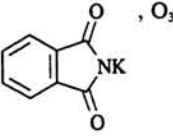
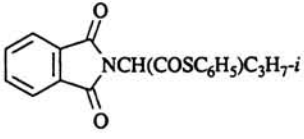
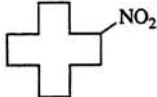
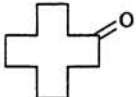
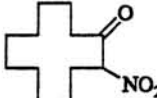
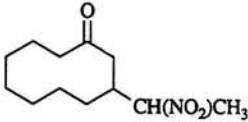
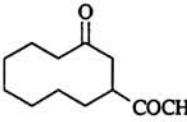
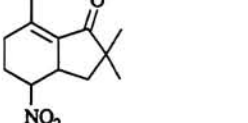
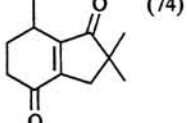

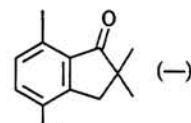
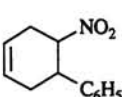
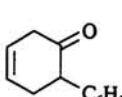
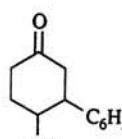
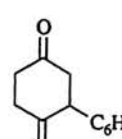
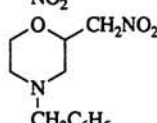
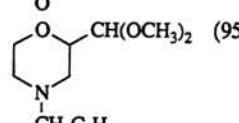
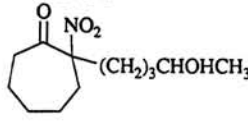
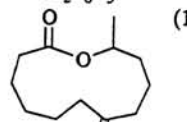
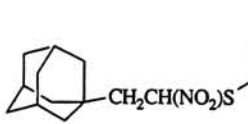
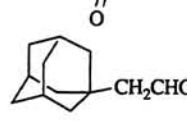
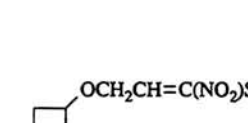
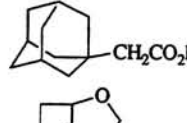
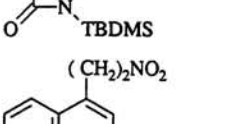
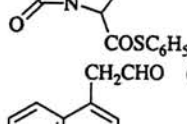
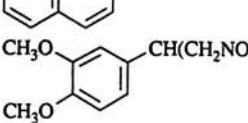
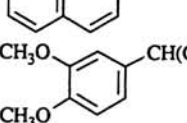


Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. NaOH 2. HCl	 (90)	320
	1. (C ₂ H ₅) ₃ N 2. C ₁₆ H ₃₃ N(CH ₃) ₃ ⁺ MnO ₄ ⁻	 (67)	261
4-NCC ₆ H ₄ C(CH ₃) ₂ CH ₂ NO ₂	1. NaOC ₄ H ₉ - <i>t</i> 2. KMnO ₄	4-NCC ₆ H ₄ C(CH ₃) ₂ CHO (83)	126
4-CH ₃ OC ₆ H ₄ CH(CH ₂ NO ₂)CH ₂ CN	1. NaOCH ₃ , CH ₃ OH 2. H ₂ SO ₄ , CH ₃ OH 3. HCl, H ₂ O	4-CH ₃ OC ₆ H ₄ CH(CHO)CH ₂ CN (60)	38
C ₆ H ₅ CO(CH ₂) ₂ CH(NO ₂)CH ₃	1. NaOH 2. H ₃ O ⁺	C ₆ H ₅ CO(CH ₂) ₂ COCH ₃ (—)	130
4-BrC ₆ H ₄ COCH=CHCH(NO ₂)CH ₃	1. NaOH 2. KMnO ₄ , MgSO ₄ Silica gel, KMnO ₄	" (—)	130
4-BrC ₆ H ₄ COCH=CHC(CH ₃)=NO ₂ Na	1. KOH 2. (CH ₃ O) ₂ SO ₂ , heat Silica gel, CH ₃ OH (NH ₄) ₂ S ₂ O ₈ Ascorbic acid, HCl	4-BrC ₆ H ₄ COCH=CHCOCH ₃ (85)	202, 203 151
C ₆ H ₅ COCH=CHCH(NO ₂)CH ₃	1. KOH 2. (CH ₃ O) ₂ SO ₂ , heat Silica gel, CH ₃ OH (NH ₄) ₂ S ₂ O ₈ Ascorbic acid, HCl	4-BrC ₆ H ₄ COCH=CHCOCH ₃ (57)	152
C ₆ H ₅ COCH=CHC(CH ₃)=NO ₂ Na	1. KOH 2. (CH ₃ O) ₂ SO ₂ , heat Silica gel, CH ₃ OH (NH ₄) ₂ S ₂ O ₈ Ascorbic acid, HCl	" (31)	152
4-O ₂ NC ₆ H ₄ COCH=CHC(CH ₃)=NO ₂ Na	1. KOH 2. (CH ₃ O) ₂ SO ₂ , heat Silica gel, CH ₃ OH Ascorbic acid, HCl	" (36)	152
CH ₃ CO(CH ₂) ₂ CH(NO ₂)C ₆ H ₁₃ - <i>n</i>	Silica gel, NaOCH ₃ Silica gel, KMnO ₄	C ₆ H ₅ COCH=CHCOCH ₃ (85)	151
	1. NaOH, C ₂ H ₅ OH 2. H ⁺	" (64)	152
C ₂ H ₅ CH=CH(CH ₂) ₂ CO(CH ₂) ₂ CH(NO ₂)-CH ₃	1. (C ₂ H ₅) ₃ N 2. C ₁₆ H ₃₃ N(CH ₃) ₃ ⁺ MnO ₄ ⁻	" (—)	321
CH ₂ =CH(CH ₂) ₉ NO ₂	1. NaOH 2. H ₂ SO ₄	" (64)	261
	1. NaOC ₄ H ₉ - <i>t</i> 2. KMnO ₄	C ₂ H ₅ CH=CH(CH ₂) ₂ CO(CH ₂) ₂ COCH ₃ (72)	319
	1. KOH, CH ₃ OH 2. KMnO ₄ , MgSO ₄	CH ₂ =CH(CH ₂) ₈ CHO (59)	127
	1. (C ₂ H ₅) ₃ N 2. C ₁₆ H ₃₃ N(CH ₃) ₃ ⁺ MnO ₄ ⁻	" (50)	131
C ₆ H ₅ (CH ₂) ₅ NO ₂	1. ZnCl ₂ , HCl 2. CH ₃ OH, H ⁺	" (66)	261
OHCC(C ₆ H ₅)=CHC(CH ₃)=NO ₂ Na	Silica gel, CH ₃ OH TiCl ₃ , H ₂ O	C ₆ H ₅ (CH ₂) ₄ CH(OCH ₃) ₂ (—)	182
C ₂ H ₅ C≡C(CH ₂) ₂ CH(NO ₂)(CH ₂) ₂ COCH ₃	NaH ₂ PO ₂ , RaNi, H ⁺	OHCC(C ₆ H ₅)=CHCOCH ₃ (46)	152
C ₆ H ₅ CH=CHCH=C(NO ₂)CH ₃	1. NaOH, C ₂ H ₅ OH 2. H ₂ SO ₄ , H ₂ O, C ₃ H ₁₂	C ₂ H ₅ C≡C(CH ₂) ₂ CO(CH ₂) ₂ COCH ₃ (85)	153, 154
C ₆ H ₅ CH ₂ CH(NO ₂)C ₃ H ₇ - <i>n</i>	1. DBU, TMSCl 2. MCPBA	C ₆ H ₅ CH ₂ CH=CHCOCH ₃ (64)	226
C ₆ H ₅ CH(CH ₂ CO ₂ CH ₃)CH(NO ₂)CH ₃	(<i>n</i> -C ₄ H ₉) ₄ N ⁺ Br ⁻ , CH ₃ CN, O ₂ , e ⁻	C ₆ H ₅ CH ₂ COC ₃ H ₇ - <i>n</i> (93)	267
CH ₃ CH(NO ₂)CH(C ₆ H ₅)CH ₂ CO ₂ CH ₃	C ₂ H ₅ OH, NaOCH ₃ , e ⁻	C ₆ H ₅ CH(CH ₂ CO ₂ CH ₃)COCH ₃ (70)	143b
<i>n</i> -C ₇ H ₁₅ CH(NO ₂)(CH ₂) ₂ CO ₂ C ₂ H ₅	1. NaOH 2. H ₂ SO ₄	CH ₃ COCH(C ₆ H ₅)CH ₂ CO ₂ CH ₂ (68)	194
CH ₃ CONHC(CO ₂ C ₂ H ₅) ₂ (CH ₂) ₂ CH-(CH ₂ NO ₂)O ₂ CCH ₃		<i>n</i> -C ₇ H ₁₅ CO(CH ₂) ₂ CO ₂ C ₂ H ₅ (72)	193
<i>i</i> -C ₃ H ₇ CH=C(NO ₂)SC ₆ H ₅		CH ₃ CONHC(CO ₂ C ₂ H ₅) ₂ (CH ₂) ₂ CH(CHO)-O ₂ CCH ₃ (—)	322
		 (46)	313

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
C ₁₂ 	1. NaOC ₄ H ₉ -t 2. KMnO ₄	 (91)	127
	H ₂ O ₂ , K ₂ CO ₃ , CH ₃ OH	HO ₂ C(CH ₂) ₁₀ CO ₂ H (92)	266a
	1. NaOH, CH ₃ OH 2. H ₂ SO ₄		(95) 323
	1. NaOC ₂ H ₅ , C ₂ H ₅ OH 2. HCl 3. TsOH, heat	 (74)	324
		 (—)	
	1. NaOC ₂ H ₅ , C ₂ H ₅ OH 2. HCl		325
	1. NaOC ₂ H ₅ , C ₂ H ₅ OH 2. HCl	 (43)	326
	1. NaOCH ₃ , CH ₃ OH 2. H ₂ SO ₄ , CH ₃ OH	 (95)	327
	1. KH, heat 2. dil HCl	 (18)	102
	TiCl ₃	 (68)	229
	TiCl ₃ (excess)	 (95)	229
	1. (n-C ₄ H ₉) ₄ N ⁺ F ⁻ 2. O ₃	 (56)	143a
	1. NaOH, C ₂ H ₅ OH 2. H ₂ SO ₄ , H ₂ O, C ₅ H ₁₂	 (54)	267
	1. NaOCH ₃ , CH ₃ OH 2. H ₂ SO ₄ , CH ₃ OH 3. dil HCl		(73) 38

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TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

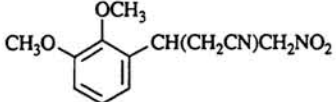
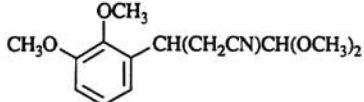

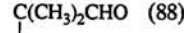
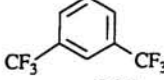
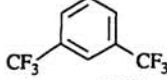
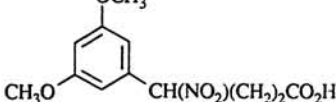
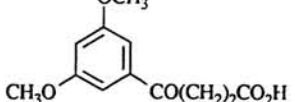
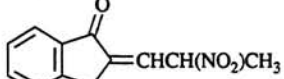
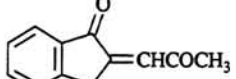
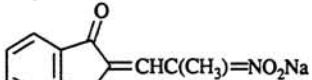
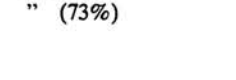
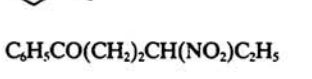
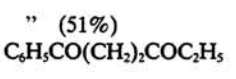
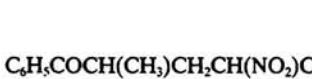
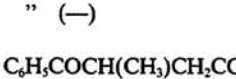
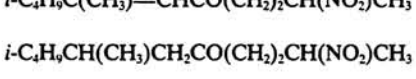
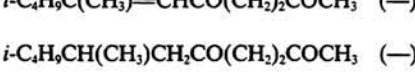


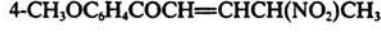
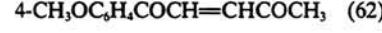




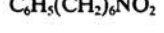

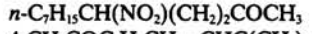
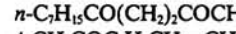
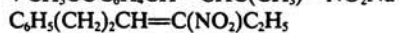
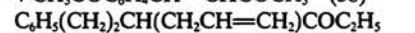


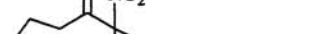

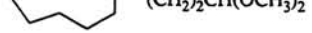


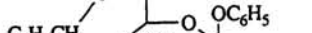

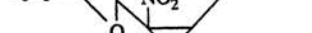

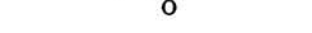
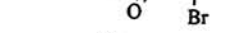

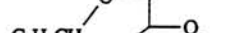
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. NaOCH ₃ , CH ₃ OH 2. H ₂ SO ₄ , CH ₃ OH	 (90)	39
	1. NaOC ₄ H ₉ - <i>t</i> 2. KMnO ₄	 (88)	126, 127
	1. NaOH, C ₂ H ₅ OH 2. HCl	 (90)	328
	1. NaOH, C ₂ H ₅ OH 2. HCl	 (56)	151
	1. KOH 2. (NH ₄) ₂ S ₂ O ₈		152
	Silica gel, CH ₃ OH	 (73%)	152
	(NH ₄) ₂ S ₂ O ₈ 1. NaOH 2. H ₃ O ⁺	 (51%)	152
	1. NaOH 2. KMnO ₄ , MgSO ₄ Silica gel, KMnO ₄	 (71)	202, 203
	1. NaOH 2. KMnO ₄	 (—)	129
	1. NaOH 2. KMnO ₄	 (—)	129
	1. KOH 2. (CH ₃ O) ₂ SO ₂ , heat	 (62)	151
	Silica gel, CH ₃ OH (NH ₄) ₂ S ₂ O ₈	 (41)	152
	Ascorbic acid, HCl	 (19)	152
	1. ZnCl ₂ , HCl 2. H ₂ O	 (26)	152
	CH ₃ OH, NaO ₂ CH, e ⁻	 (50)	182
	Silica gel, CH ₃ OH	 (87-90)	193
	1. CH ₂ =CHCH ₂ TMS, AlCl ₃ 2. TiCl ₃ , CH ₃ O(CH ₂) ₂ OCH ₃	 (38)	152
	1. NaOCH ₃ , CH ₃ OH 2. TiCl ₃ , NaOAc	 (50)	157
		 (82)	315
			
	LiBr	 (77)	234
	LiN ₃	 (76)	234
		 (100)	116
	1. OH ⁻ 2. KMnO ₄		

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

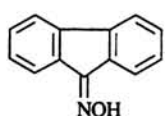
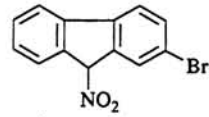
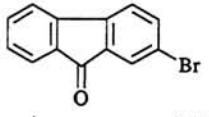
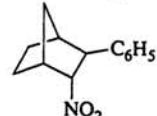
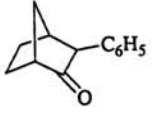
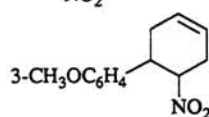
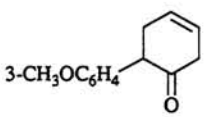
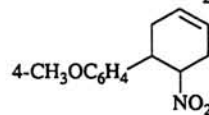
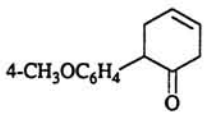
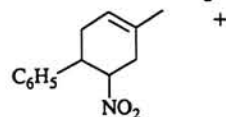
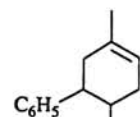
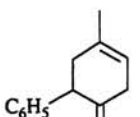
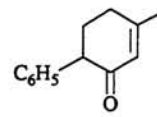
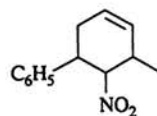
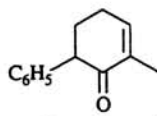
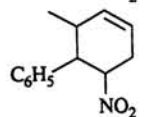
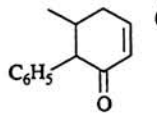
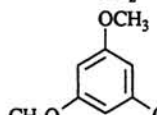
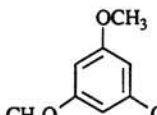
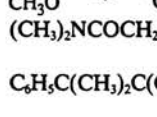
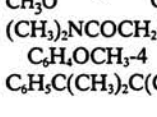
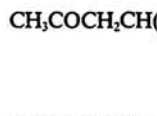
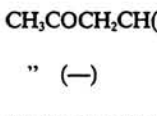
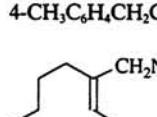
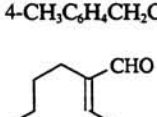
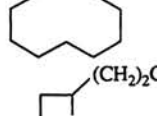
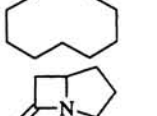
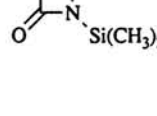
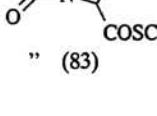




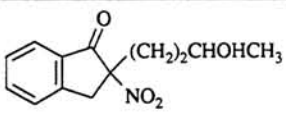
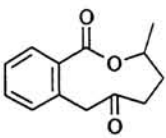
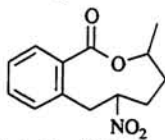
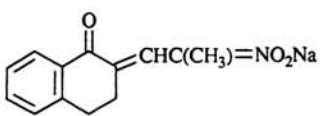
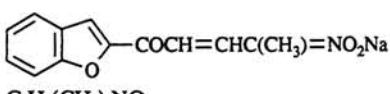
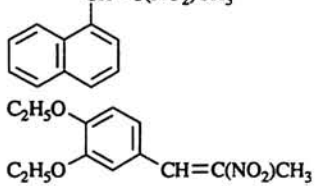
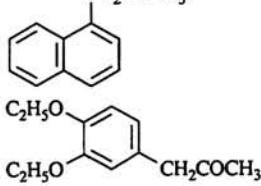
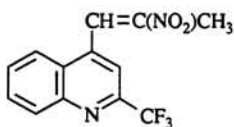
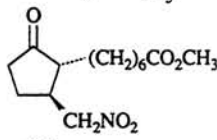
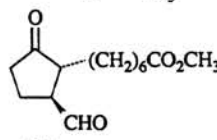
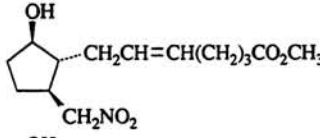
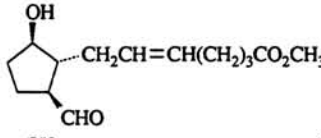
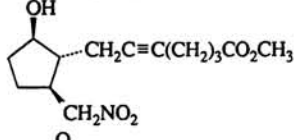
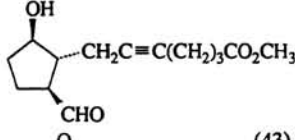
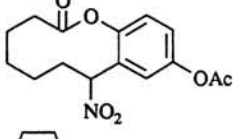
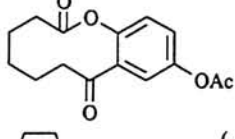
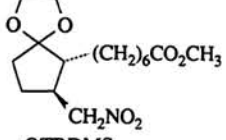
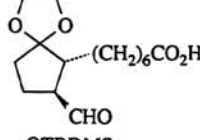
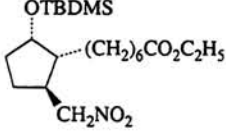
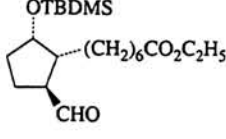
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	KOH, (NH ₄) ₂ S ₂ O ₈	" (72)	150
	1. KOH	" (90)	329
	2. Air	" (62%) + 	(24) 244
	hν, CH ₃ OH or <i>t</i> -C ₄ H ₉ OH		
	1. KOC ₂ H ₅ 2. Air		(-) 137
	1. NaOH 2. HCl		(71-D) 292
	1. NaOC ₂ H ₅ , C ₂ H ₅ OH 2. HCl		(87) 325
	"		(88) 325
 + 	"	 + 	(65) + (15) 326
	"		(35) 326
	"		(33) 326
	1. NaOH 2. HCl		(70) 328
	1. NaOCH ₃ , CH ₃ OH 2. H ₂ SO ₄ , CH ₃ OH		CH ₃ O-COCH(CH ₃)CH ₂ CO ₂ H (CH ₃) ₂ NCOCH ₂ CH[CH(OCH ₃) ₂]- C ₆ H ₄ OCH ₃ -4 (15) 330
	1. NaOC ₄ H ₉ - <i>t</i> 2. KMnO ₄		C ₆ H ₅ C(CH ₃) ₂ C(CH ₃) ₂ CHO (88) 126, 127
	1. NaOH 2. H ₃ O ⁺		CH ₃ COCH ₂ CH(C ₆ H ₅)COC ₂ H ₅ (-) 130
	1. NaOH 2. KMnO ₄ , MgSO ₄		" (-) 130
	1. LiOCH ₃ 2. KMnO ₄ , buffer		4-CH ₃ C ₆ H ₄ CH ₂ CO(CH ₂) ₂ COCH ₃ (85) 331
	1. NaOCH ₃ 2. TiCl ₃		CHO (79) 291
	1. HF, Py 2. KOC ₄ H ₉ - <i>t</i> 3. O ₃		(83) 143
	1. (<i>n</i> -C ₄ H ₉) ₄ N ⁺ F ⁻ 2. O ₃		" (83) 143a

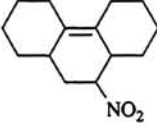
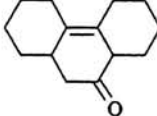
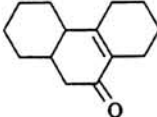
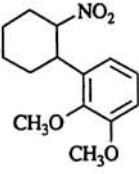
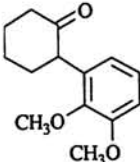
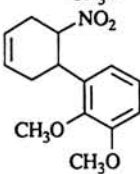
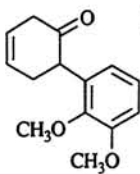
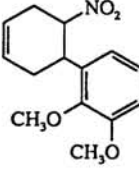
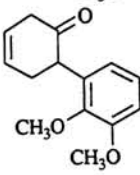
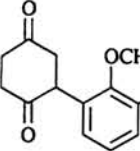
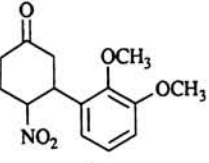
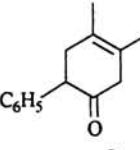
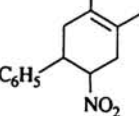
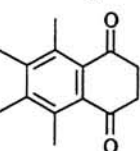
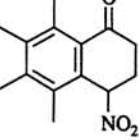
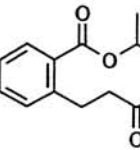
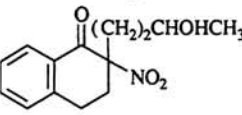
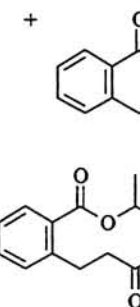
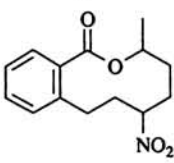
TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	KH	 I (13)	332
		+  II (32)	
	$n\text{-(C}_4\text{H}_9)_4\text{N}^+\text{F}^-$ Silica gel, CH ₃ OH	I (7) + II (43) (44)	332 152
	(NH ₄) ₂ S ₂ O ₈ Silica gel, CH ₃ OH	" (17) (36)	152 152
$\text{C}_6\text{H}_5(\text{CH}_2)_7\text{NO}_2$ $\text{CH}_3\text{COCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}(\text{NO}_2)\text{C}_2\text{H}_5$ $\text{CH}=\text{C}(\text{NO}_2)\text{CH}_3$	ZnCl ₂ , HCl KMnO ₄ , silica gel 1. LiHB(C ₄ H ₉ -s) ₃ 2. H ₂ SO ₄	$\text{C}_6\text{H}_5(\text{CH}_2)_6\text{CHO}$ (53) $\text{CH}_3\text{COCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{COC}_2\text{H}_5$ (72) CH_2COCH_3 (81)	182 202, 203 224
	"	 (83)	224
	NaH ₂ PO ₂ , RaNi, H ⁺	CH_2COCH_3 (86)	226
	1. NaOCH ₃ , CH ₃ OH 2. H ₂ SO ₄	 (71)	333
	"	 (56)	333
	"	 (>36)	333
	1. Py, Ac ₂ O, heat 2. Ice 3. dil HCl	 (43)	101
	1. KOH, MgSO ₄ 2. KMnO ₄	 (-)	125
	1. NaOCH ₃ , CH ₃ OH 2. O ₃ , DMS	 (71-82)	334

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TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
C ₁₄ 	1. NaOC ₂ H ₅ , C ₂ H ₅ OH 2. HCl	 (—)	335
	1. NaOH, C ₂ H ₅ OH 2. HCl	 (—)	335, 336
	"	 (35)	337
	"	 (—) +  (—)	337
	"	 (83)	325
	"	 (17)	337
	"	 (50)	325
	1. KOH, CH ₃ OH 2. KMnO ₄ , MgSO ₄	 (100)	338
	KH	 (22)	332
	(n-C ₄ H ₉) ₄ N ⁺ F ⁻	 (30) +  (<1)	332

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TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	H_2O_2, K_2CO_3, CH_3OH	+ (34)	266a
	1. $NaOC_2H_5, C_2H_5OH$ 2. HCl	(69)	326
			326
		+ (99 total)	326
	$NaNO_2, n-C_3H_7ONO, DMSO$	(90)	198
	1. HF, Py 2. KOC_4H_9-t 3. O_3	(53)	143
	1. $n-(C_4H_9)_4N^+F^-$ 2. O_3	(83)	143a
	1. $n-(C_4H_9)_4N^+F^-$ 2. O_3	(79)	143a
	1. $n-(C_4H_9)_4N^+F^-$ 2. O_3	(31)	143a
	1. HF, Py 2. KOC_4H_9-t 3. O_3	(64)	143
$3,4,5-(CH_3O)_3C_6H_2COCH=CH-C(CH_3)=NO_2Na$	Silica gel, CH_3OH	$3,4,5-(CH_3O)_3C_6H_2COCH=CHCOCH_3$ (58)	152
$C_6H_5COC(CO_2C_2H_5)=CHC(CH_3)=NO_2Na$	$(NH_4)_2S_2O_8$ Silica gel, CH_3OH	" (39)	152
	1. $Py, Ac_2O, heat$ 2. Ice 3. $dil HCl$	$C_6H_5COC(CO_2C_2H_5)=CHCOCH_3$ (-) (49)	152 101

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

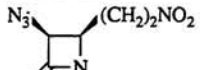
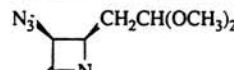
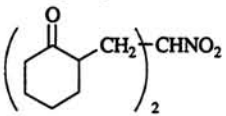
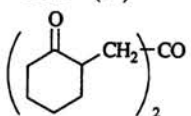
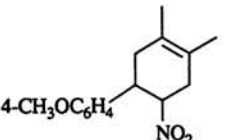
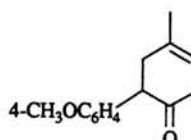
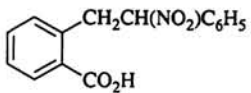
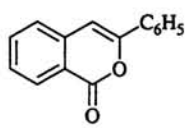

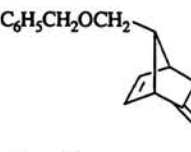
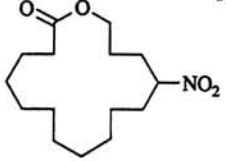
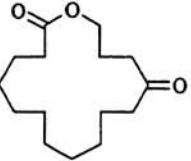
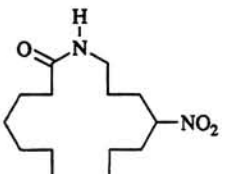
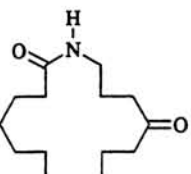
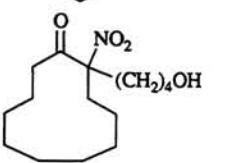
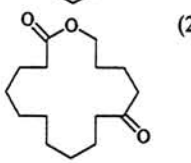
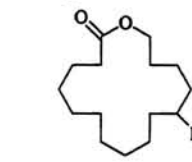
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. NaOCH ₃ 2. H ₂ SO ₄ , CH ₃ OH	 (95)	43
$n\text{-C}_{10}\text{H}_{21}\text{CH}=\text{C}(\text{NO}_2)\text{C}_2\text{H}_5$	1. CH ₂ =CHCH ₂ TMS, AlCl ₃ 2. TiCl ₃ , CH ₃ O(CH ₂) ₂ OCH ₃	$n\text{-C}_{10}\text{H}_{21}\text{CH}(\text{CH}_2\text{CH}=\text{CH}_2)\text{COC}_2\text{H}_5$ (74)	157
$\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{NO}_2)\text{C}_6\text{H}_5$	1. CH ₂ =C(CH ₃)CH ₂ TMS, AlCl ₃ 2. NaOCH ₃ , CH ₃ OH, TiCl ₃ , NH ₄ OAc	$n\text{-C}_{10}\text{H}_{21}\text{CH}(\text{COC}_2\text{H}_5)\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$ (74)	157
	1. NaCH(CO ₂ C ₂ H ₅) 2. H ⁺	(C ₂ H ₅ O ₂ C) ₂ CHCH(C ₆ H ₅)COC ₆ H ₅ (—)	36
C₁₅			
$n\text{-C}_{11}\text{H}_{23}\text{C}(\text{CH}_3)_2\text{CH}_2\text{NO}_2$	1. NaOC ₄ H ₉ - <i>t</i> 2. KMnO ₄	$n\text{-C}_{11}\text{H}_{23}\text{C}(\text{CH}_3)_2\text{CHO}$ (96)	126, 127
$\text{CH}_2=\text{CHCH}_2\text{C}(\text{SC}_6\text{H}_5)(\text{COCH}_3)\text{CH}(\text{CH}_3)\text{CH}_2\text{NO}_2$	1. NaOCH ₃ 2. H ₂ SO ₄	$\text{CH}_2=\text{CHCH}_2\text{C}(\text{SC}_6\text{H}_5)(\text{COCH}_3)\text{CH}(\text{CH}_3)\text{CHO}$ (81)	339
	1. NaOC ₂ H ₅ , C ₂ H ₅ OH 2. HCl	 (—)	335
	1. NaOC ₂ H ₅ , C ₂ H ₅ OH 2. HCl	 (89)	326
	1. NaOCH ₃ , CH ₃ OH 2. TiCl ₃ , NH ₄ OAc 3. H ₃ O ⁺ 4. Ac ₂ O, H ⁺	 (32)	308
	1. NaOH 2. H ₂ SO ₄ , CH ₃ OH 3. Ac ₂ O, H ⁺	" (84)	308
$\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2$ 	1. NaOCH ₃ , CH ₃ OH 2. TiCl ₃ , NH ₄ OAc	$\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2$  (64)	91
	1. (C ₂ H ₅) ₃ N 2. CAN	 (75)	98
	1. NaOCH ₃ 2. TiCl ₃ , NH ₄ OAc	" (87)	99
	1. LiOCH ₃ , Na ₂ B ₄ O ₇ 2. KMnO ₄	 (2)	136
	1. KH, heat 2. dil HCl	 (28)	102
		 (9)	

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

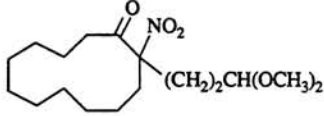
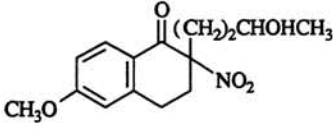
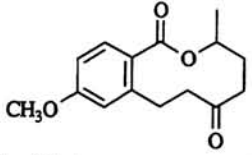

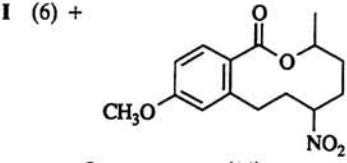
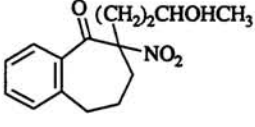
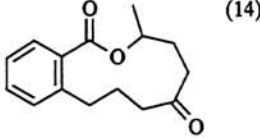
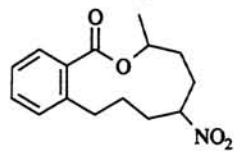
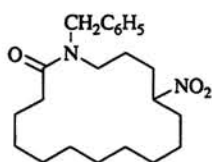
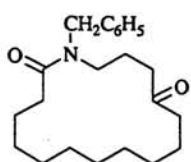
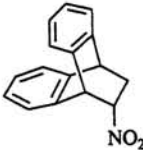
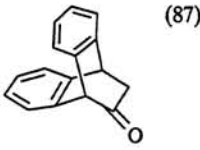
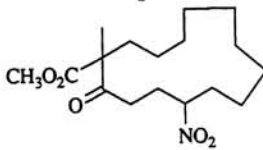
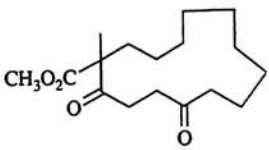
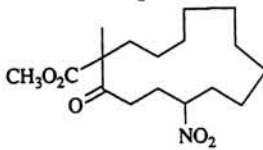
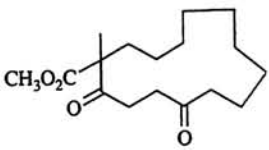
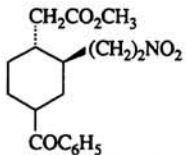
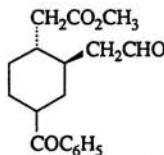
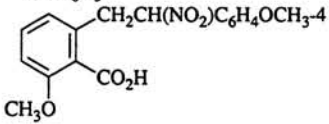
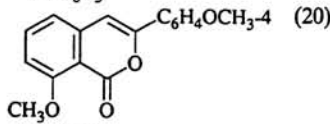
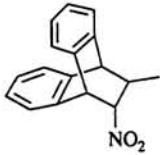
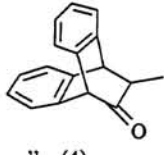

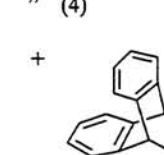
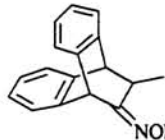
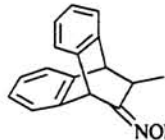
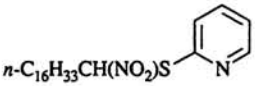
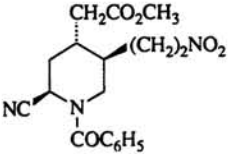
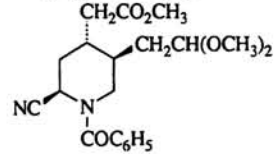
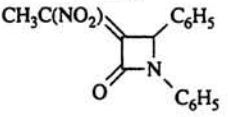
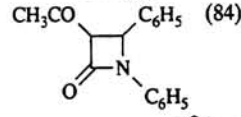
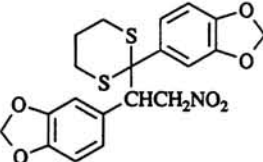
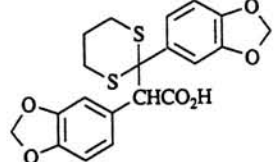
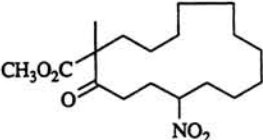
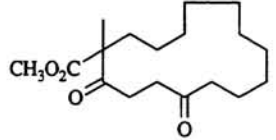
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. NaOCH ₃ , CH ₃ OH 2. TiCl ₃ , NaOAc	CH ₃ O ₂ C(CH ₂) ₁₀ CO(CH ₂) ₂ CH(OCH ₃) ₂ (83)	315
	KH	 I (59)	332
	(<i>n</i> -C ₄ H ₉) ₄ N ⁺ F ⁻	I (6) +  (33)	332
	KH	 (14) +  (45)	332
	1. LiOCH ₃ 2. TiCl ₃ , NaOAc	 (63)	136
<i>n</i> -C ₁₆ H ₃₃ NO ₂	1. NaOC ₂ H ₅ - <i>t</i> 2. KMnO ₄ "	<i>n</i> -C ₁₅ H ₃₁ CHO (87)	127
4-(C ₆ H ₅ SO ₂)C ₆ H ₄ C(CH ₃) ₂ CH ₂ NO ₂	1. NaOH 2. H ₃ O ⁺	4-(C ₆ H ₅ SO ₂)C ₆ H ₄ C(CH ₃) ₂ CHO (91)	126, 127
<i>t</i> -C ₄ H ₉ COCH ₂ CH(C ₆ H ₅)CH(NO ₂)C ₂ H ₅	1. NaOH 2. KMnO ₄ , MgSO ₄	<i>t</i> -C ₄ H ₉ COCH ₂ CH(C ₆ H ₅)COC ₂ H ₅ (-)	130
4-(C ₆ H ₅ CH ₂ O)C ₆ H ₄ CH ₂ CH(NO ₂)CH ₃	1. (<i>n</i> -C ₄ H ₉) ₃ P, (C ₆ H ₅ S) ₂ 2. H ₂ O	" (-)	130
4-(C ₆ H ₅ CH ₂ O)C ₆ H ₄ CH=C(NO ₂)CH ₃	1. C ₆ H ₅ SH, (C ₆ H ₅ S) ₂ , (C ₂ H ₅) ₃ N, (<i>n</i> -C ₄ H ₉) ₃ P 2. H ₂ O	4-(C ₆ H ₅ CH ₂ O)C ₆ H ₄ CH ₂ COCH ₃ (82)	175
	1. KOH, C ₂ H ₅ OH 2. HCl or H ₂ SO ₄	 (87)	175
	1. NaOCH ₃ 2. TiCl ₃ , NaOAc	 (83)	340
	1. NaOCH ₃ 2. TiCl ₃ , NaOAc	 (83)	262

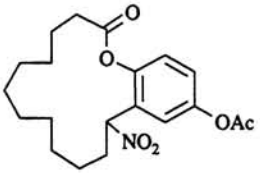
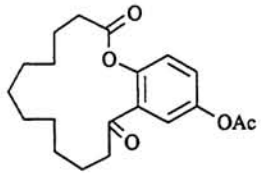
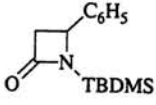
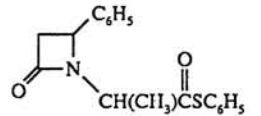
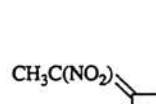
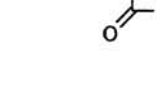
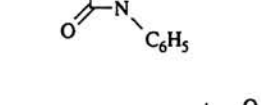
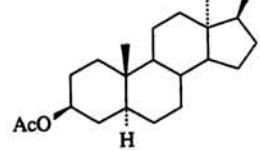
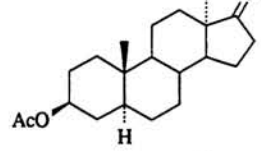
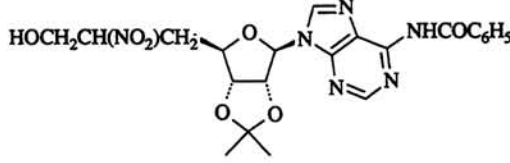
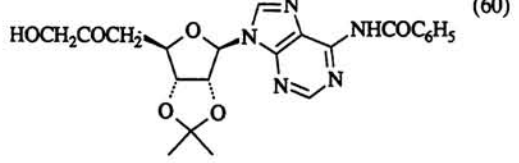
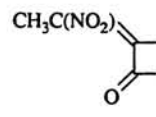
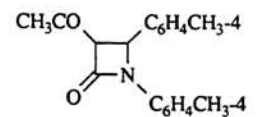
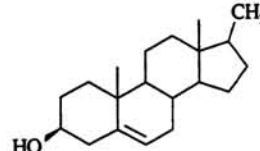
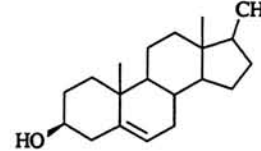
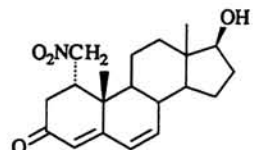
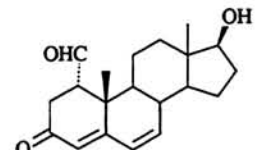
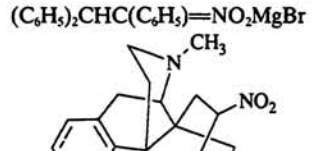
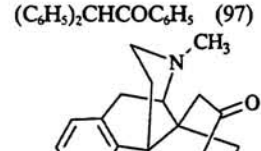
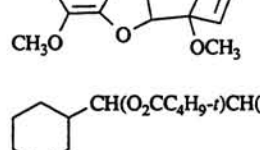
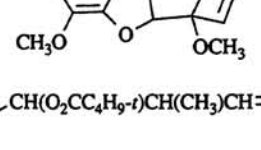


TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
C ₁₇ 	1. NaOCH ₃ , CH ₃ OH 2. H ₂ SO ₄	 (78)	33
	1. NaOCH ₃ , CH ₃ OH 2. TiCl ₃ , NH ₄ OAc 3. H ₃ O ⁺ 4. Ac ₂ O, H ⁺	 (20)	308
	1. NaOH 2. H ₂ SO ₄ , CH ₃ OH 3. Ac ₂ O, H ⁺ 1. KOH, C ₂ H ₅ OH 2. HCl or H ₂ SO ₄	 (17)	308
	1. KOH, H ₂ O, CH ₃ OH 2. HCl	 (4)	340
		+  (32)	13
C ₆ H ₅ COCH(C ₆ H ₅)CH ₂ CH(NO ₂)CH ₃ C ₆ H ₅ COCH ₂ CH(C ₆ H ₅)CH(NO ₂)CH ₃	KMnO ₄ , silica gel KMnO ₄ , silica gel	C ₆ H ₅ COCH(C ₆ H ₅)CH ₂ COCH ₃ (91) C ₆ H ₅ COCH ₂ CH(C ₆ H ₅)COCH ₃ (87)	202, 203 202, 203
	TiCl ₃ (excess)	<i>n</i> -C ₁₆ H ₃₃ CO ₂ H (100)	229
	TiCl ₃ 1. NaOCH ₃ , CH ₃ OH 2. H ₂ SO ₄	<i>n</i> -C ₁₆ H ₃₃ CHO (70)  (—)	341
	1. (<i>n</i> -C ₄ H ₉) ₃ SnH 2. O ₃ , DMS	 (84)	341
	NaNO ₂ , <i>n</i> -C ₃ H ₇ ONO, DMSO	 (90)	198
	1. NaOCH ₃ 2. TiCl ₃ , NaOAc	 (81)	262
C ₁₈ C ₆ H ₅ COCH ₂ CH(C ₆ H ₅)CH(NO ₂)C ₂ H ₅	1. NaOH 2. H ₃ O ⁺	C ₆ H ₅ COCH ₂ CH(C ₆ H ₅)COC ₂ H ₅ (—)	130
	1. NaOH 2. KMnO ₄ , MgSO ₄	" (—)	130
	KMnO ₄ , silica gel	" (83)	202, 203

772

773

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. Py, Ac ₂ O, heat 2. Ice 3. dil HCl	 (57)	101
	1. (n-C ₄ H ₉) ₄ N ⁺ F ⁻ , CH ₃ CH=C(NO ₂)SC ₆ H ₅ 2. O ₃	 (75)	143a
	1. KOC ₄ H ₉ -t 2. O ₃	" (41)	143a
	1. (n-C ₄ H ₉) ₃ SnH 2. O ₃ , DMS	CH ₃ CO  (91)	341
	NaOC ₂ H ₅ , hv	 (55)	239
	1. NaOCH ₃ 2. TiCl ₃ , pH 5	 (60)	342
	1. (n-C ₄ H ₉) ₃ SnH 2. O ₃ , DMS	CH ₃ CO  (80)	341
	TMBG, MIBA	 (41)	149
	TiCl ₃ , H ₂ O	 (—)	163
	HCl 1. LiAlH ₄ 2. HCl, H ₂ O	 (97)	343
	HCl 1. LiAlH ₄ 2. HCl, H ₂ O	 (62)	186
	1. NaOCH ₃ 2. TiCl ₃	 (65)	344

774

C₁₉

775

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. NaOCH ₃ 2. TiCl ₃ , NH ₄ OAc, H ₂ O		(70) 160, 253
	1. NaOCH ₃ 2. TiCl ₃ , NH ₄ OAc, H ₂ O		" (72) 345
	1. (C ₆ H ₅) ₃ P 2. TiCl ₃ , NH ₄ OAc		(16) 253
	1. NaOCH ₃ , CH ₃ OH 2. O ₃		(75) 346
	NaOC ₂ H ₅ , hv		(22) 239
	1. (n-C ₄ H ₉) ₃ SnH 2. HF, CH ₃ OH		(tr) 341
			(45) 341
	1. LDA 2. MoO ₅ ·Py·HMPA		(96) 145
	1. KOH, C ₂ H ₅ OH 2. HCl or H ₂ SO ₄		" (56) 340
	1. NaOCH ₃ , CH ₃ OH 2. TiCl ₃ , NaOAc, H ₂ O		(60) 159
	1. DBU, TMSCl 2. MCPBA		(-) 143b

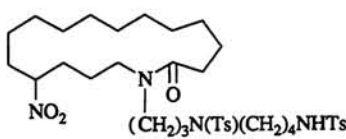
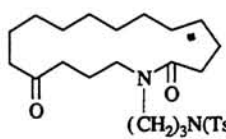
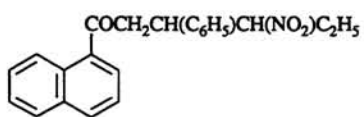
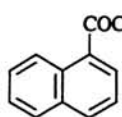
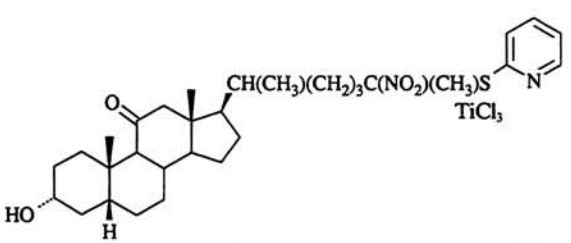
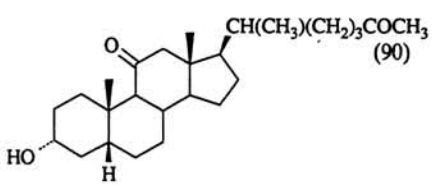
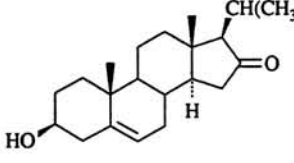
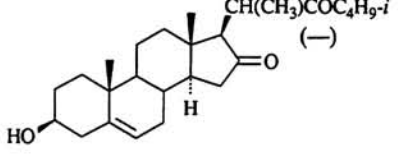
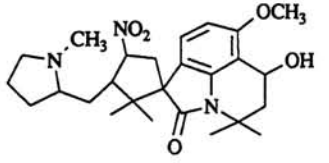
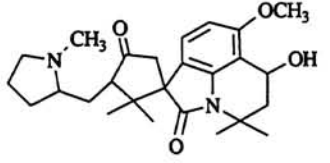
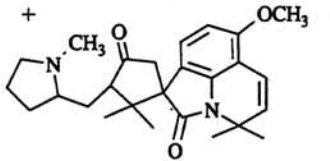
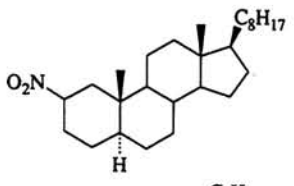
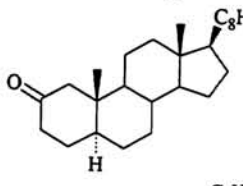
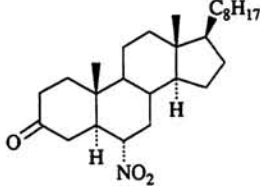
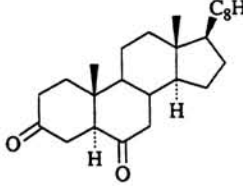
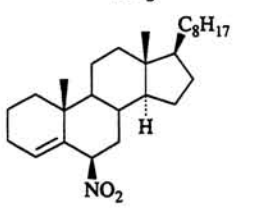
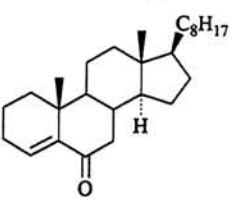
776

 C₂₁

777

 C₂₂

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
<p>C₂₃</p> 	<p>1. NaOCH₃, CH₃OH 2. TiCl₃, NaOAc, H₂O</p>	 (60)	159
<p>C₂₄</p> 	<p>1. NaOH 2. H₃O⁺</p>	 COCH ₂ CH(C ₆ H ₅)COC ₂ H ₅ (—)	130
<p>C₂₅</p> 	<p>1. NaOH 2. KMnO₄, MgSO₄</p>	 CH(CH ₃)(CH ₂) ₃ COCH ₃ (90)	229
<p>C₂₆</p> 	<p>1. NaOH 2. H₂SO₄</p>	 CH(CH ₃)COC ₄ H _{9-i} (—)	347
<p>C₂₇</p> 	<p>1. KOH, CH₃OH 2. H₂SO₄</p>	 (28) +  (46)	82
<p>C₂₈</p> 	<p>1. KOH, C₂H₅OH 2. H₂SO₄</p>	 C ₈ H ₁₇ (60)	44
<p>C₂₉</p> 	TMBG, MIBA	 C ₈ H ₁₇ (78)	149
<p>C₃₀</p> 	TMBG, MIBA	 C ₈ H ₁₇ (58)	149

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TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

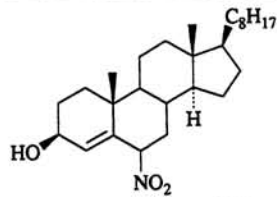
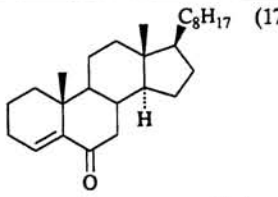
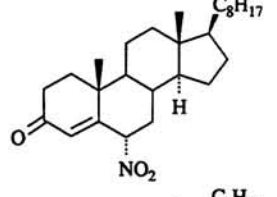
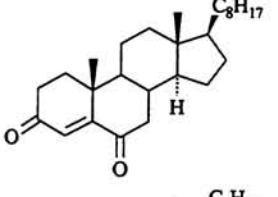
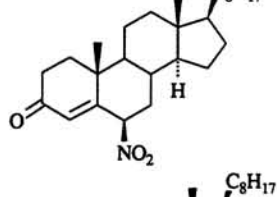
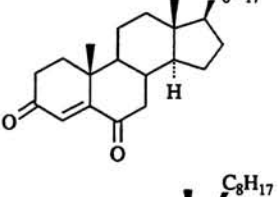
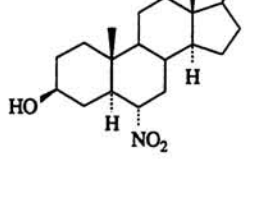
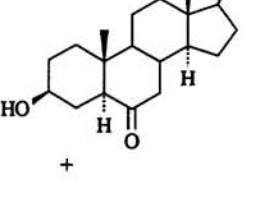
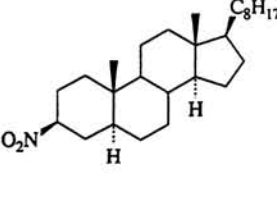
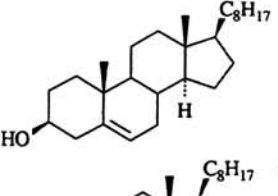
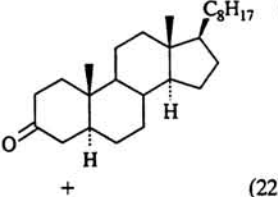
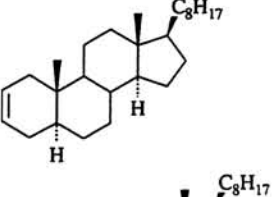
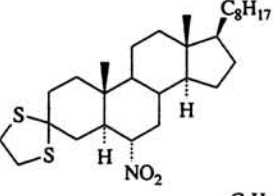
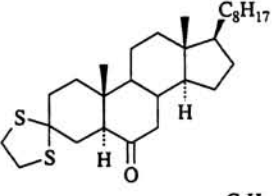
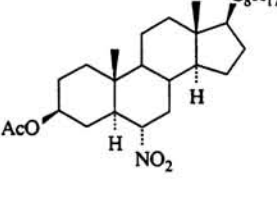
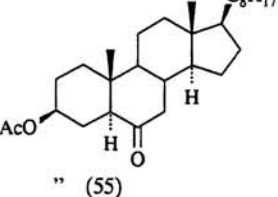
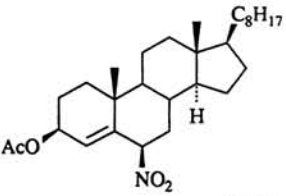
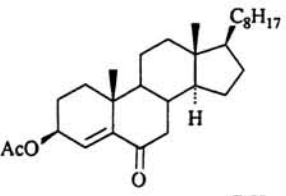
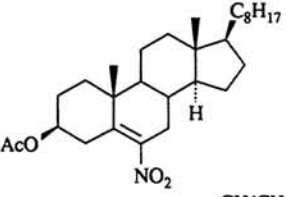
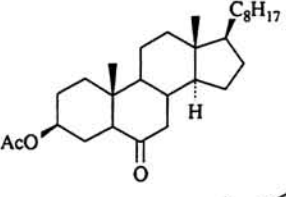
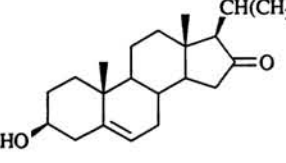
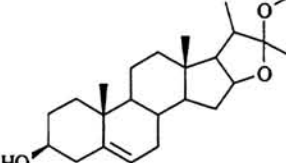

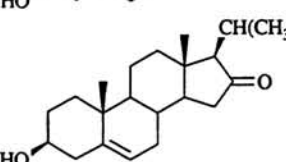
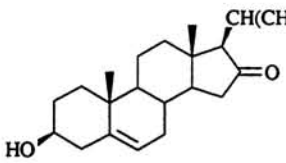
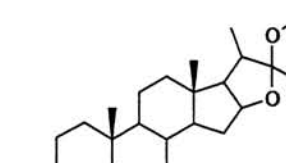
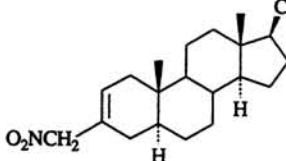
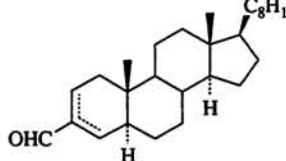
Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	CrCl ₃ , HCl, Zn	 (17)	174
	CrCl ₃ , HCl, Zn	 (97)	174
	CrCl ₃ , HCl, Zn	 (100)	174
	NaOC ₂ H ₅ , hv	 (22)	239
	NaOC ₂ H ₅ , hv	 (18)  (16) +  (22)	239
	TMBG, MIBA	 (89)	149
	TMBG, MIBA	 (95)	149
	1. (n-C ₄ H ₉) ₃ P, (C ₆ H ₅ S) ₂ 2. H ₂ O	" (55)	175

TABLE I. NEF REACTION OF NITRO COMPOUNDS (Continued)

Nitro Compound	Reagents	Product(s) and Yield(s) (%)	Refs.
	CrCl ₃ , HCl, Zn	 (75)	174
	NaHPO ₂ , Ra Ni, H ⁺	 (52)	226
	CH(CH ₃)CH(NO ₂)(CH ₂) ₂ CH(CH ₃)CH ₂ OAc 1. NaBH ₄ , C ₂ H ₅ OH 2. HCl	 (86)	347, 348
	1. NaOH 2. H ₂ SO ₄ or KMnO ₄	 CH(CH ₃)CO(CH ₂) ₂ CH(CH ₃)CH ₂ OAc (20)	347, 348
	CH(CH ₃)CH(NO ₂)(CH ₂) ₂ CH(CH ₂ OAc) ₂ 1. NaBH ₄ , C ₂ H ₅ OH 2. HCl	 CH ₂ OH (83)	349
	TMBG, MIBA	 C ₈ H ₁₇ (33-D)	149

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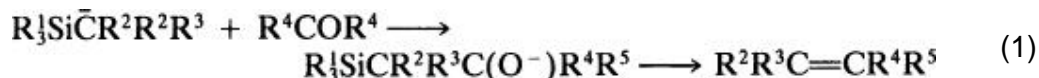
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The Peterson Olefination Reaction

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1. Introduction

The Peterson olefination reaction provides a useful method for the preparation of alkenes from α -silyl carbanions and carbonyl compounds. As alkenes hold a pivotal role in synthetic methodology for the introduction of



vicinal functionality, particularly in a stereoselective manner, (1) the Peterson reaction is increasing in importance in the reaction repertoire. This chapter discusses the reaction (Eq. 1) and its advantages over comparable methods such as the Wittig reaction.

Although elimination of β -silylalkoxides, as shown in Eq. 1, was noted in 1947, (2) it was not until Peterson described the preparation of functionalized alkenes from α -silyl carbanions in 1968 that the full potential of the reaction became apparent. (3) Alkenes are usually only isolated directly from the condensation when an anion-stabilizing group is present in the carbanion (R^2 or R^3 in Eq. 1); if not, the β -hydroxysilane is formed. Many examples of the formation of alkenes from β -hydroxysilanes are cited in the literature. These eliminations are discussed in this chapter, although they strictly should not be called Peterson olefination reactions. However, the "common" organic reactions of β -hydroxysilanes which follow the usual pathways—such as the thermolytic elimination of esters derived from those alcohols (4)—are omitted.

The central nature of the Peterson reaction to organosilicon chemistry has led all reviews in this area to discuss the subject to some extent. (5-22) In addition, the reaction itself has been reviewed previously. (23, 24)

2. Mechanism

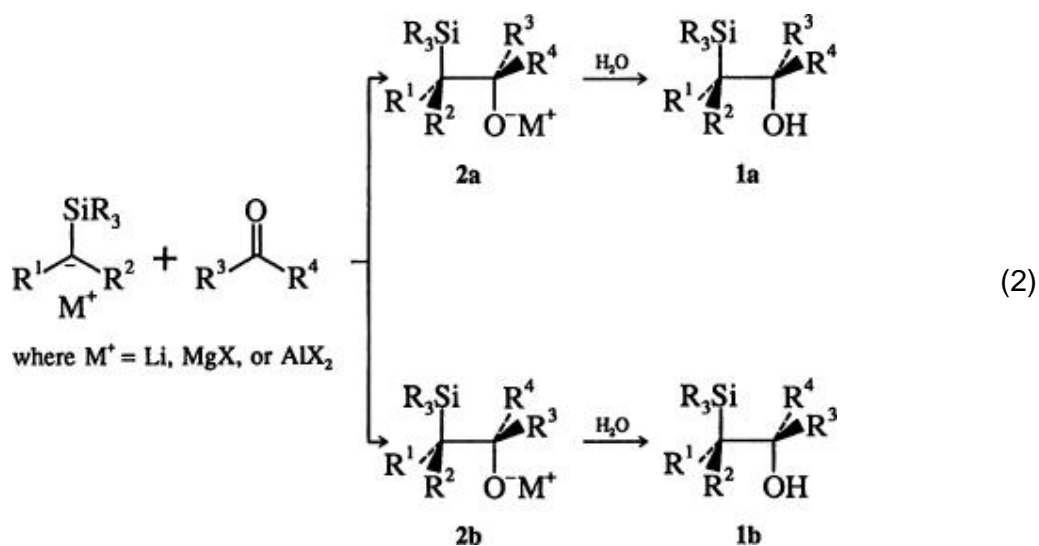
At present, the exact mechanism of the Peterson reaction is not clear. The experimental results can, however, be rationalized and used in a predictive manner, particularly with regard to the *E:Z* product ratio, by consideration of α -silyl carbanions bearing alkyl or electron-donating substituents and those with electron-withdrawing groups separately. The principal mechanistic difference arises from the exact timing for the elimination of the oxygen moiety—whether it is concerted with the loss of the silyl group, or stepwise (E_{1cb} -like) in nature. Indeed, CNDO–MO calculations suggest that a stepwise mechanism is plausible for the Peterson olefination reaction. (25)

2.1. Alkyl Substituents

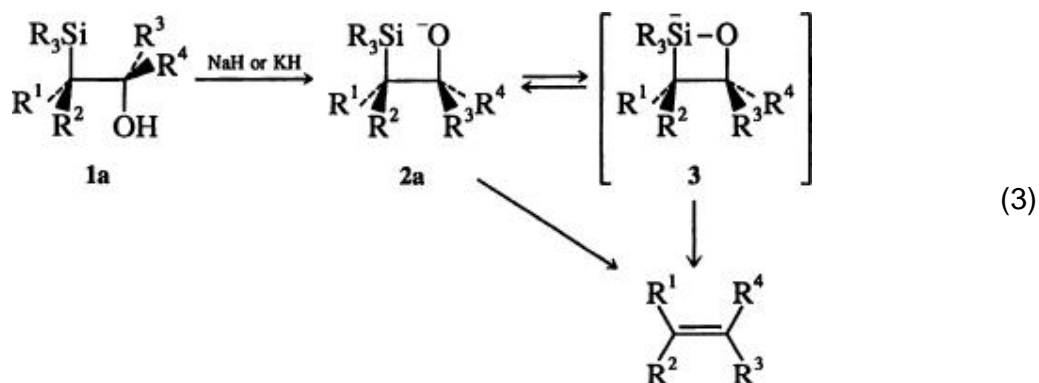
When only alkyl, hydrogen, or electron-donating substituents are present on the carbon atom bonded to silicon, the stereochemical outcome of the Peterson olefination reaction can be controlled by the choice of conditions for the elimination from the intermediate β -hydroxysilane **1**. Since aryl substituents in the α -silyl carbanion often necessitate the use of harsh conditions for the deprotonation of the parent silane, these substituents are best considered with electron-withdrawing groups.

Condensation of an α -silyl carbanion with a carbonyl compound results in a β -silylalkoxide **2**. If the metal counterion is covalently bound to the oxygen—as with lithium, magnesium, or aluminum (**3**, **26**)—then protonation provides the β -hydroxysilanes **1** which can be isolated. The condensation, however, usually results in a diastereomeric mixture of these β -hydroxysilanes, although they can be separated by the usual physical methods such as chromatography.

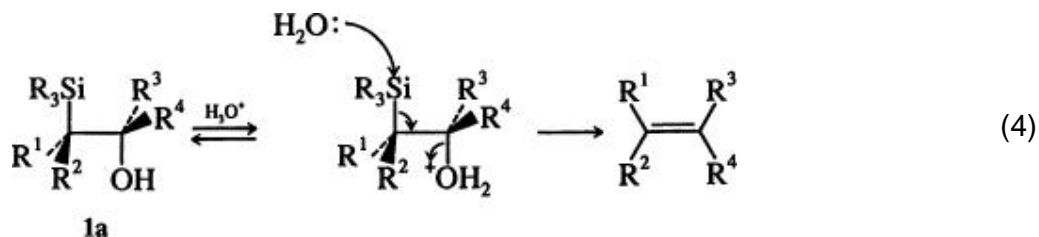
When a β -hydroxysilane (e.g., **1a**) is treated with a base to yield an alkoxide **2a** with considerable ionic character on the oxygen atom such as with a sodium or potassium counterion, or if the condensation (Eq. **2**) results in such a



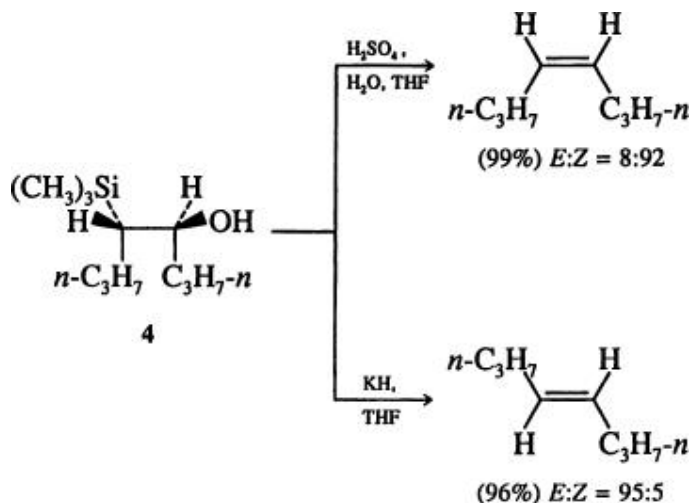
species, a *syn* elimination results. (27) A pentacoordinate silicon species **3** may be involved in the reaction, but the formation of this intermediate is still open to question (Eq. 3). This base-promoted elimination pathway is accepted as concerted to account for the stereochemical outcome observed.



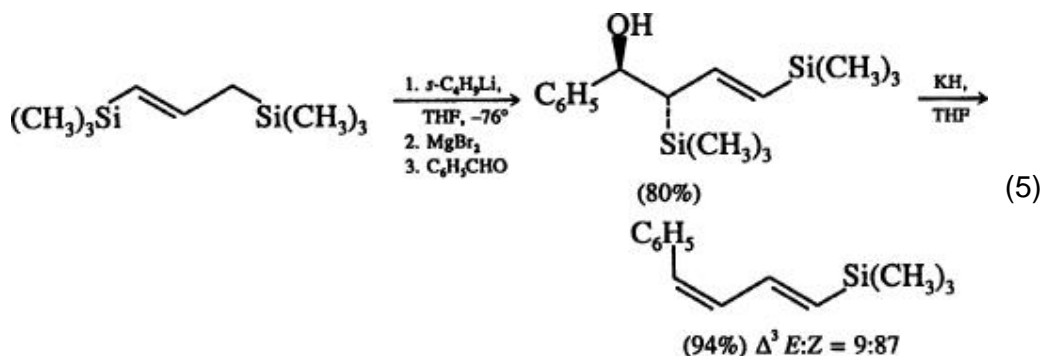
In contrast, treatment of the β -hydroxysilane **1a** with acid provides the other alkene isomer by an *anti* elimination pathway.



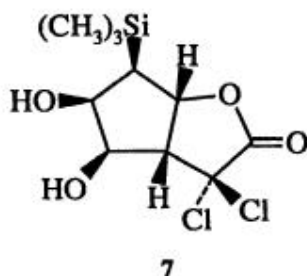
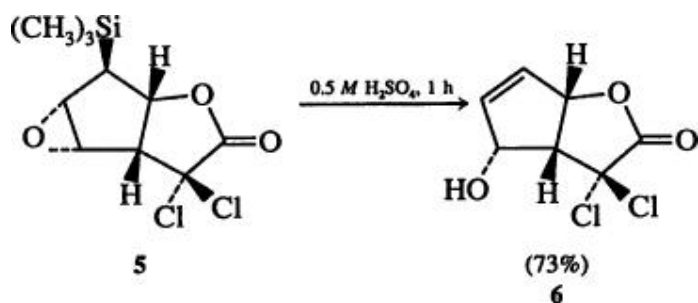
Thus either alkene is available from each diastereomer of a β -hydroxysilane **4**. (27) To achieve a stereospecific preparation of an alkene, it is necessary to



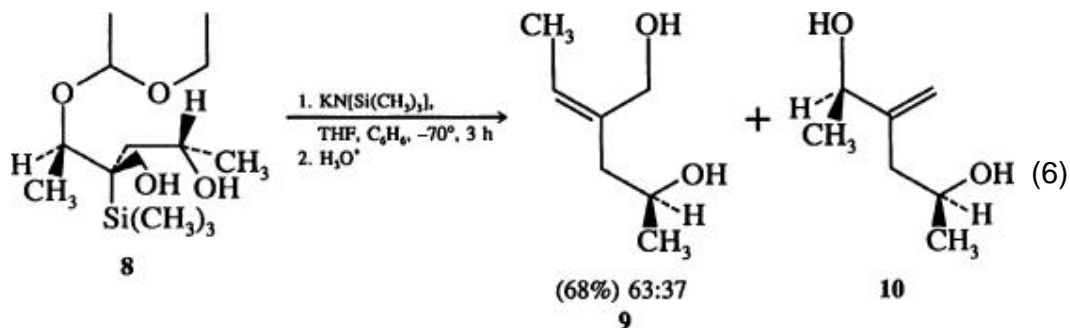
perform the condensation of the α -silyl carbanion and carbonyl compound to provide the mixture of β -hydroxysilanes **1a** and **1b** (Eq. 2). The diastereomers must then be separated and one treated with acid, the other with base, to give the required alkene isomer. To overcome this problem, stereoselective routes to α -hydroxysilanes have been developed, many of which rely upon the stereochemical consequences associated with a particular system (Eq. 5). (28)



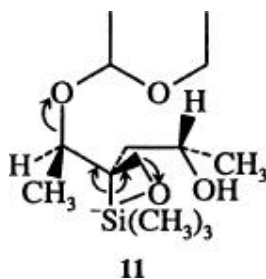
Cyclic systems can impose stereochemical constraints which do not allow the oxygen and silicon atoms to adopt the required geometry for elimination to occur. (29-32) The epoxide **5** gives the allyl alcohol **6** as its silyl ether upon standing at room temperature, or more rapidly by treatment with dilute sulfuric acid. In contrast, the diol **7** is stable to acid, base, and fluoride ion. (33)



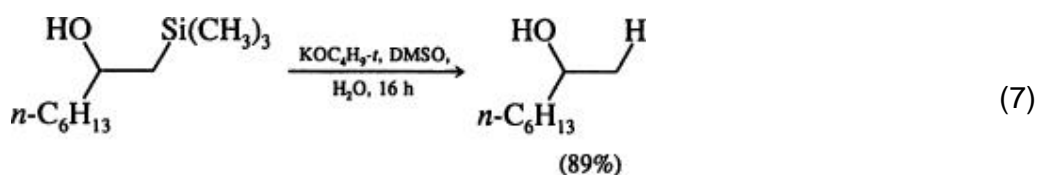
Another consequence of relative stereochemistry becomes apparent when a second leaving group is available in the system. Addition of potassium bis(trimethylsilyl)amide to the alcohol **8** results, after aqueous workup, chromatography, and removal of protecting groups, in a mixture of the allyl alcohols **9** and **10**. (34) As the alcohol **9** is the major product, the *anti* elimination



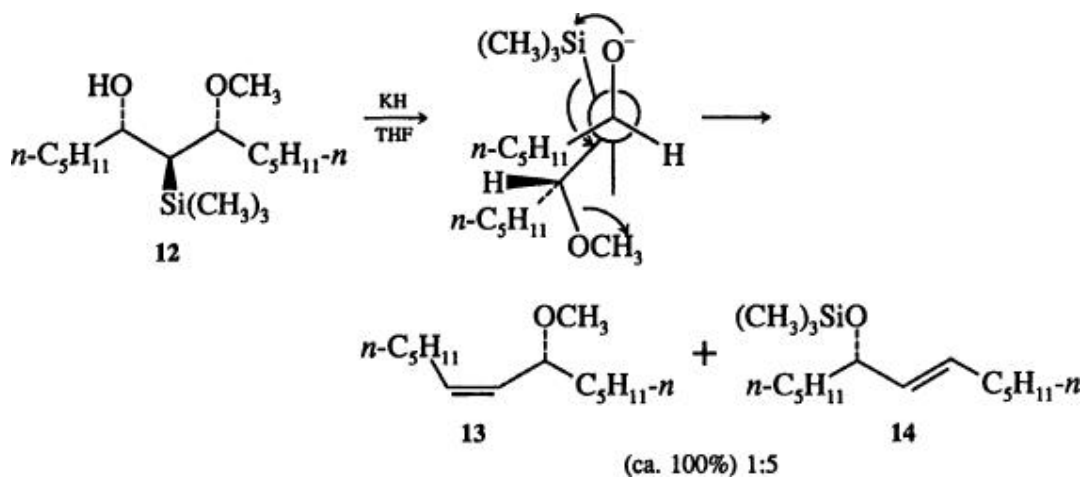
with loss of alkoxide takes place preferentially over the *syn* pathway. These observations may be rationalized either by formation of a pentacoordinate silicon species **11**, the geometry required for facile alkoxide elimination, or by transfer of the silicon from carbon to oxygen with concurrent formation of a carbanion (E_{1cb} mechanism) which then eliminates. As alkoxide elimination



affords only the *Z* isomer **9**, the formation of a “free” carbanion seems unlikely. A reaction which probably occurs by a similar mechanism is the protodesilylation of a β -hydroxysilane (Eq. 7). This substitution reaction proceeds at a rate faster than the competing elimination. (35)

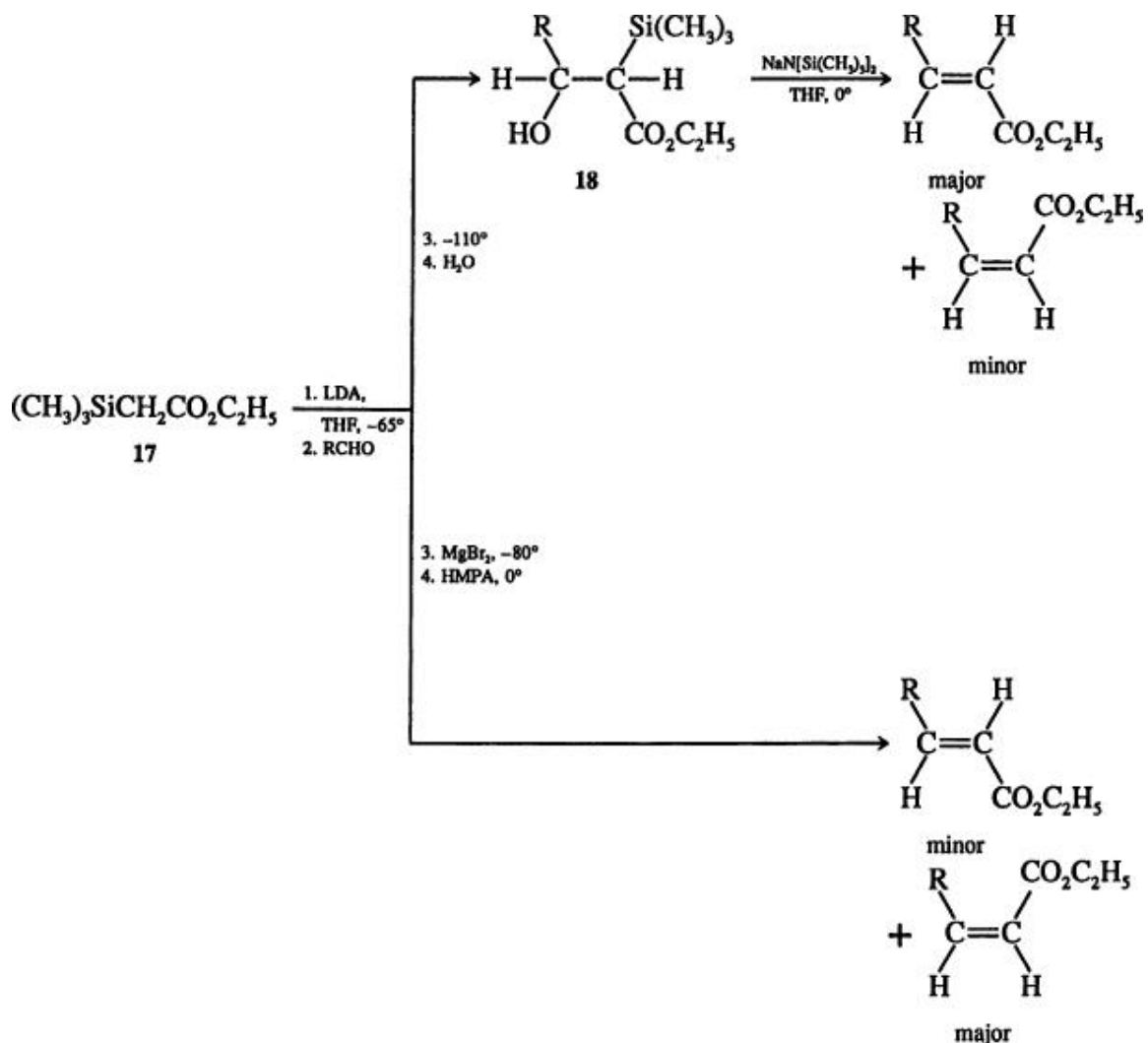


A reaction similar to that of Eq. 6 is observed with the 8-*O*-methyl ether of 6,7-*erythro*-7,8-*erythro*-7-trimethylsilyltridecane-6,8-diol (**12**). Treatment of this alcohol **12** with potassium hydride yields the *Z* alkene **13** by a Peterson *syn* elimination, but the major product is the protected allyl alcohol **14** formed by an E_2 mechanism. (36)



2.2. Electron-Withdrawing Substituents

The presence of an aryl group in conjugation with the α -silyl carbanion leads to direct formation of the alkene, and the intermediate β -hydroxysilane cannot

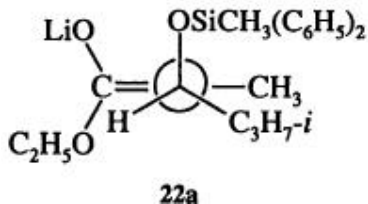
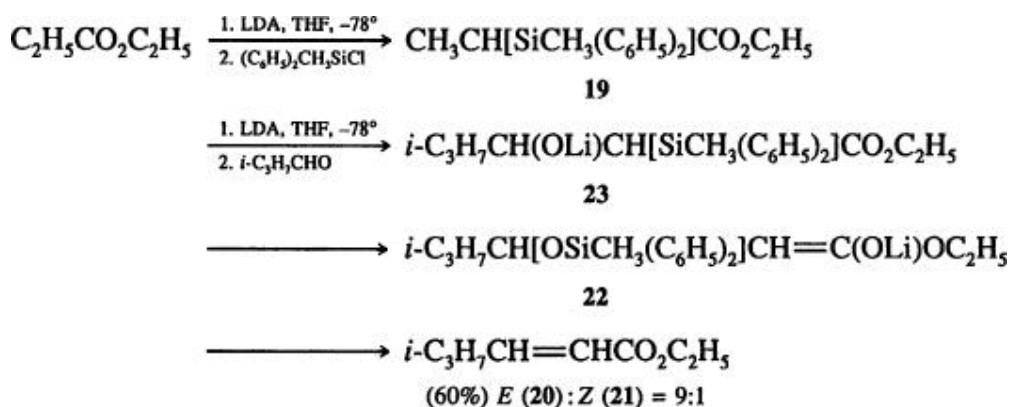


(9)

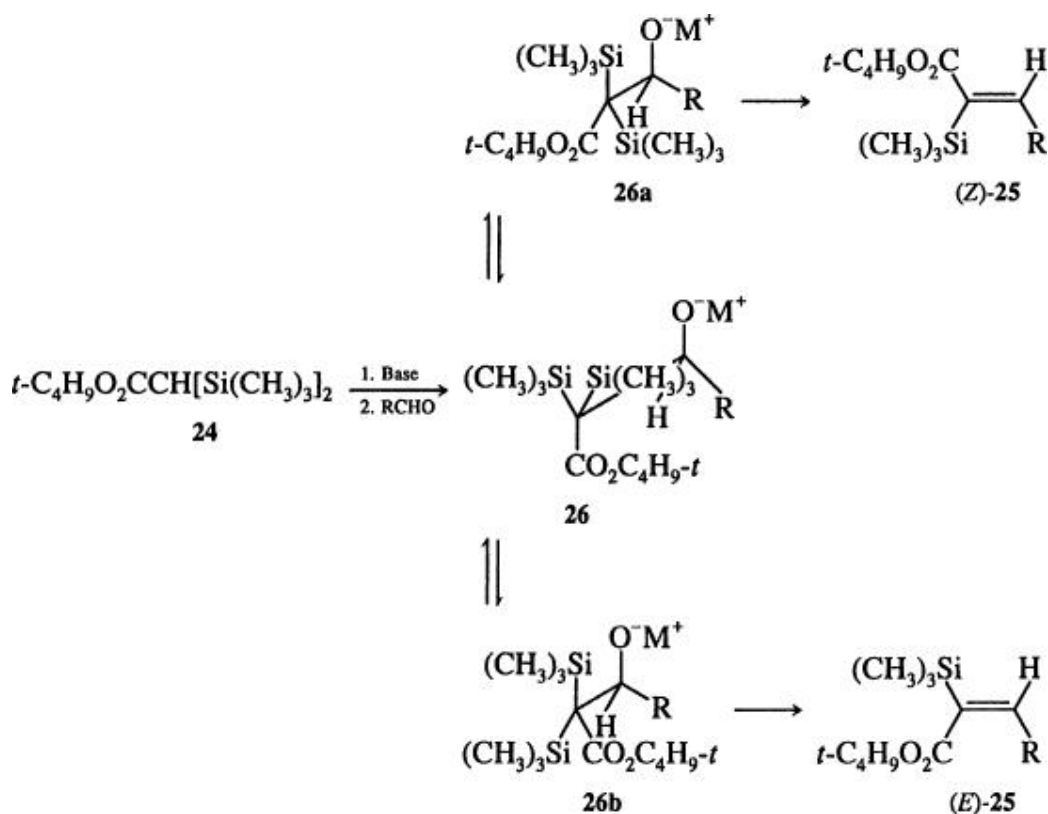
The stereoselectivity observed with the preparation of α , β -unsaturated esters has been attributed to the relative stabilities of the rotamers of the ester enolates, (42, 43) and not to the geometry of the enolate or its mode of condensation. (44) Reaction of the lithium enolate derived from ethyl (diphenylmethylsilyl) propionate (19) with 2-methylpropanal results in a 60% yield of the unsaturated esters 20 and 21 in a 9:1 ratio. (43) The product distribution is derived from the rotamer 22a of the intermediate enolate 22, which is more stable than 22b. An alternative argument is that the stereoselectivity is controlled by formation of the kinetically preferred β -hydroxysilane 23, which is followed by a synchronous *syn* elimination. (44, 45)

Reaction of enolates derived from *tert*-butyl bis(trimethylsilyl)acetate (24) with aldehydes yield the α -trimethylsilyl- α , β -unsaturated esters 25. The

stereochemical outcome of this reaction is dependent upon both the size of the alkyl group in the aldehyde and the metal counterion. The larger the alkyl

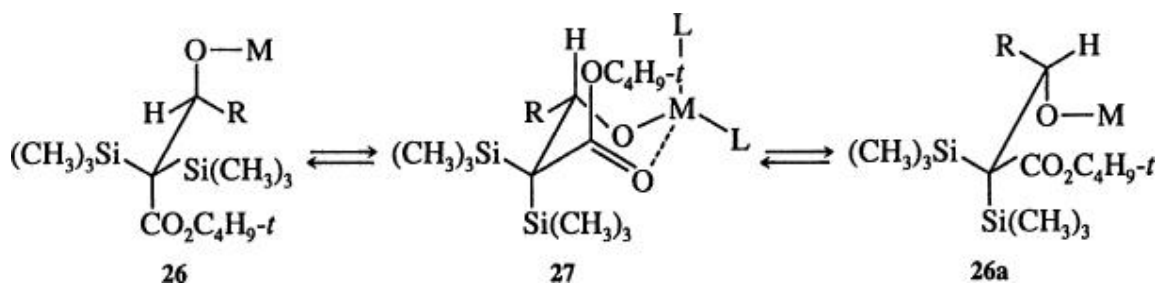


group (*R*), the greater the selectivity observed. Counterions which impart considerable ionic character to the metal–oxygen bond lead preferentially to the thermodynamically more stable product (*E*)-**25**. In contrast, relatively covalent metal enolates form the other isomer (*Z*)-**25** selectively. A mechanistic rationale is that either of the silyl groups can become *syn* to the alkoxide **26a** or **26b**. The preferred direction of rotation is governed by the nonbonding interactions with the alkyl group *R*; the larger this group, the greater the preference for counterclockwise rotation and formation of the *E* isomer. With a covalent enolate, formation of the chelate **27** is possible which,



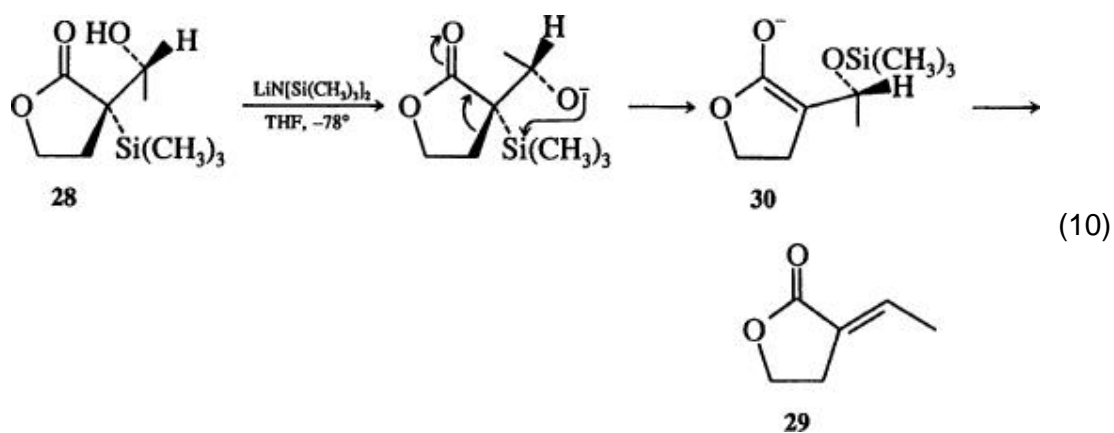
if a least-motion pathway is assumed, leads preferentially to the conformer **26a** and the *Z* isomer. (46)

In some examples, there is considerable evidence that a two-step elimination mechanism occurs. The lactone **28** reacts with lithium hexamethyldisilazide to give the α , β -unsaturated lactone **29**. The intermediate **30**, the enolate

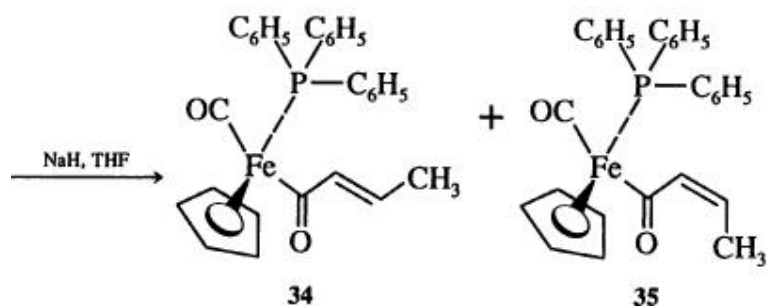
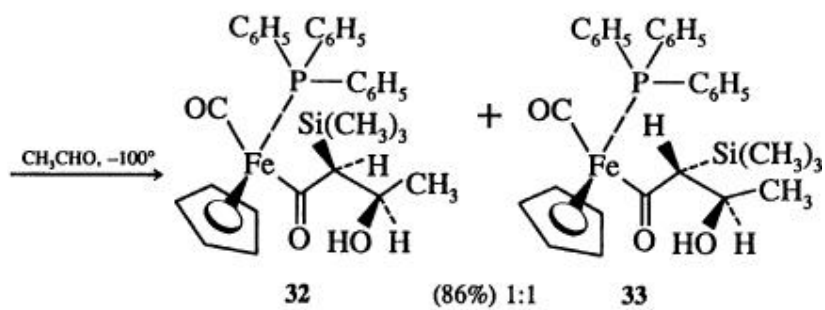
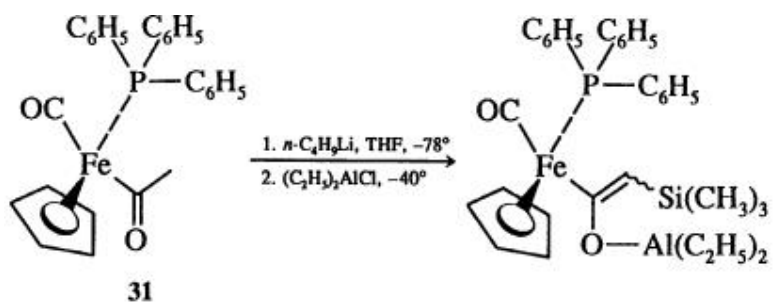


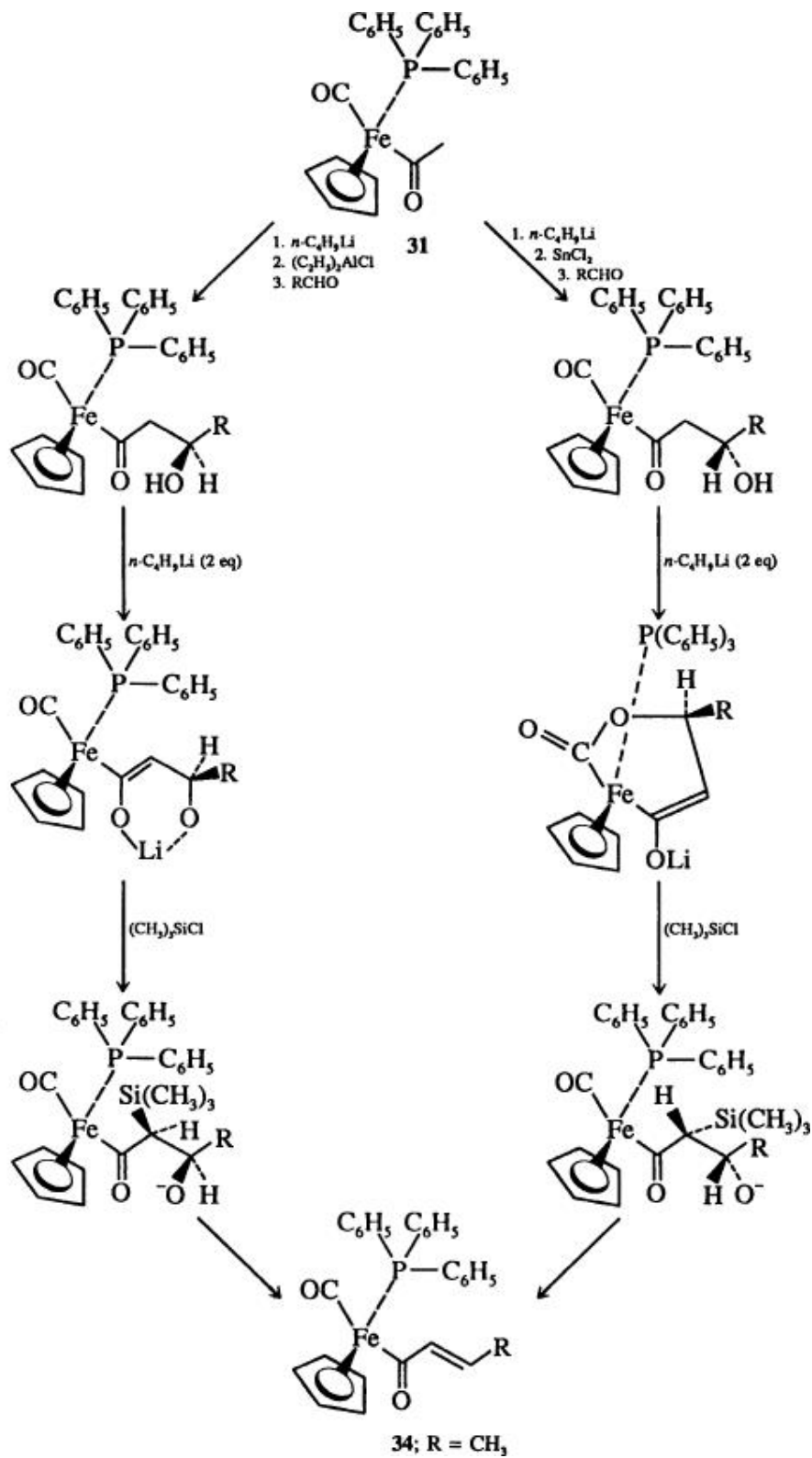
of 4,5-dihydro-3-[1-(trimethylsiloxy)ethyl]-2(3*H*)-furanone, can be detected and disappears as the reaction proceeds. The silyl ether **30** is also formed by treatment of the β -hydroxysilane **28** with a catalytic amount of base. (47)

In certain cases, the initial condensation of the α -silyl carbanion may be controlled by the presence of α -heteroatom substituents (chelation control) in the carbonyl moiety. (48-50)



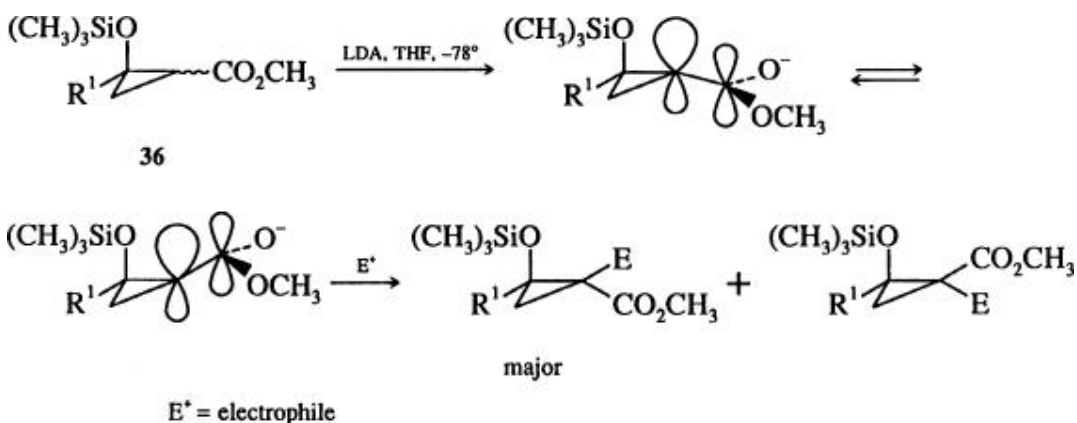
Condensation of the aluminum enolate obtained from the organoiron complex **31** with acetaldehyde affords a 1:1 mixture of the diastereomeric β -silylalcohols **32** and **33**. Only these two diastereomers, of the four possible, are formed. Base-catalyzed elimination from alcohols **32** and **33** results in a mixture of the enones **34** and **35** by *syn* elimination. (51)





Alkene **34** can be prepared selectively by stereochemical control of the silylation of the β -hydroxycarbonyl enolate from the unhindered face. (51)

When a two-step mechanism is invoked for the elimination, it is not only necessary for the silicon and oxygen atoms to adopt a favorable conformation, but the subsequent silanoxide elimination also has stereochemical requirements. The ester enolate of cyclopropane **36** does not eliminate, but can undergo reactions with electrophiles; the product ratio is a function of the stability of the configurationally labile pyramidal ester enolate. (52)



These arguments may be used to explain experimental observations, but it can still be difficult to apply them for the prediction of the stereochemical outcome of a specific reaction. (45) The exact mechanism of the Peterson olefination reaction still requires elucidation. Considerable evidence exists, however, to suggest that the elimination is not concerted but follows a two-step mechanism: attack of the alkoxide at silicon transfers the silyl group from carbon to oxygen, which is followed by elimination of silanoxide. With α -silylcarbonyl compounds, the intermediate carbanion is stabilized as an enolate (Eq. 10). A pentacoordinate silicon atom may also be invoked in the reaction (Eq. 3). Protodesilylation is consistent with this two-step mechanism (Eq. 7), (35) while the formation of diols from α , β -epoxysilanes suggests that an *anti* elimination can occur under basic conditions. (53)

3. Scope and Limitations

To be a useful reaction for the stereoselective synthesis of alkenes, the Peterson reaction requires the stereospecific preparation of β -hydroxysilanes. As the presence of an electron-withdrawing group alpha to the silyl group promotes formation of the alkene under the conditions used for the condensation of the α -silyl carbanion with the carbonyl compound, the major thrust in the stereoselective preparation of β -hydroxysilanes has been with alkyl-substituted derivatives.

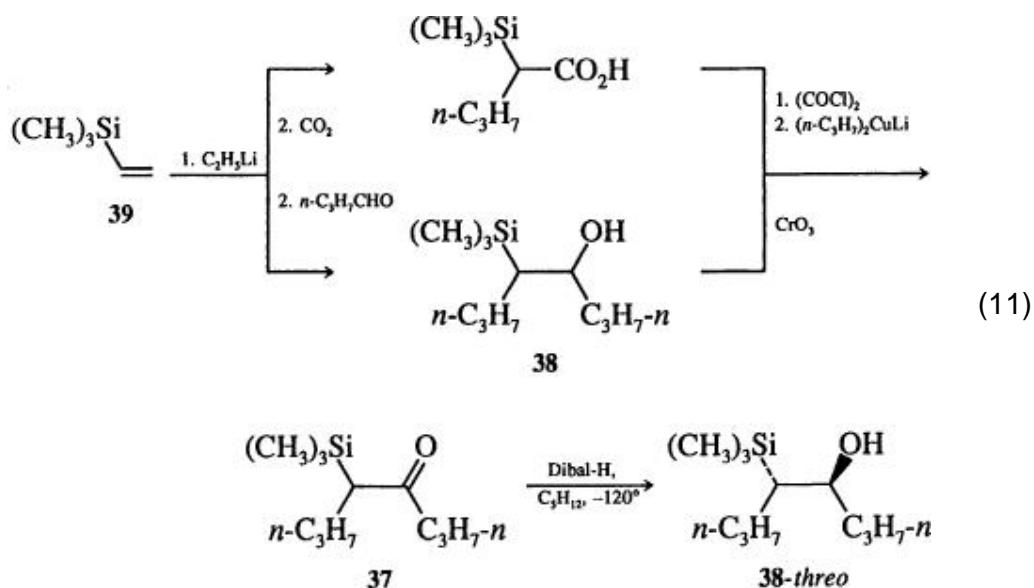
The success of the Peterson olefination reaction is dependent on the availability of α -silyl carbanions. Until recently, this was not a trivial problem to overcome—particularly for the formation of α -silyl carbanions substituted by alkyl groups alone.

3.1. Diastereoselective Synthesis of β -Hydroxysilanes

The stereoselectivity of the Peterson olefination reaction in the preparation of hydrocarbon alkenes depends upon the availability of just one β -hydroxysilane diastereomer. Thus, routes have been developed to overcome this shortcoming. In the strictest sense, these methods do not employ an α -silyl carbanion condensation with a carbonyl group and are therefore not Peterson olefination reactions. These routes do, however, expand the chemistry of β -hydroxysilanes and are included for that reason.

3.1.1.1. From α -Silyl Ketones

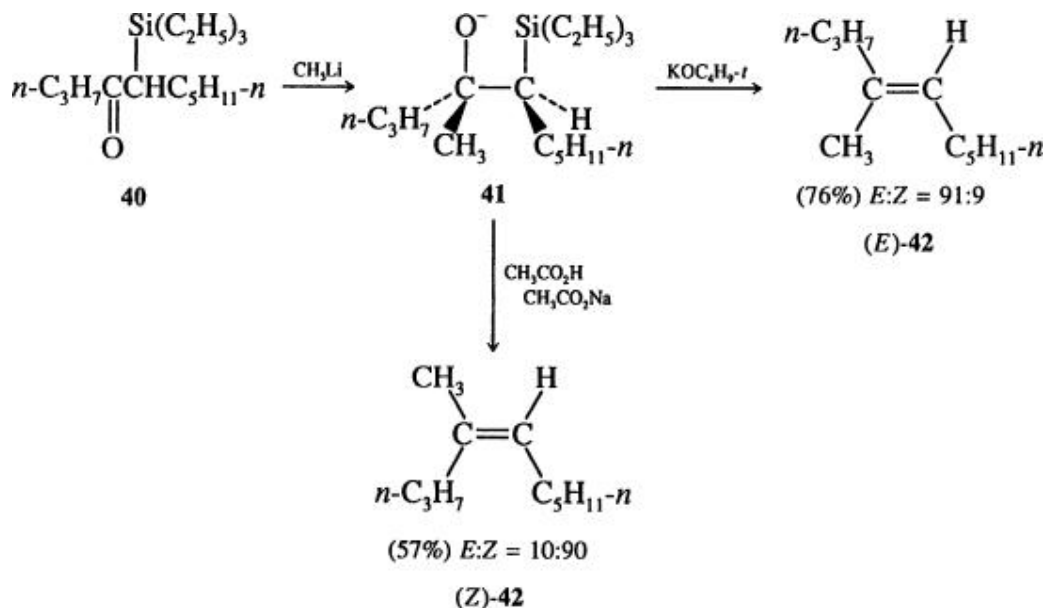
Reduction of the α -silyl ketone **37**, prepared as shown in Eq. 11, with diisobutylaluminum hydride (Dibal-H) follows Cram's rule (54) to give the *threo* isomer **38-threo** of the β -hydroxysilane **38**. (26, 27)



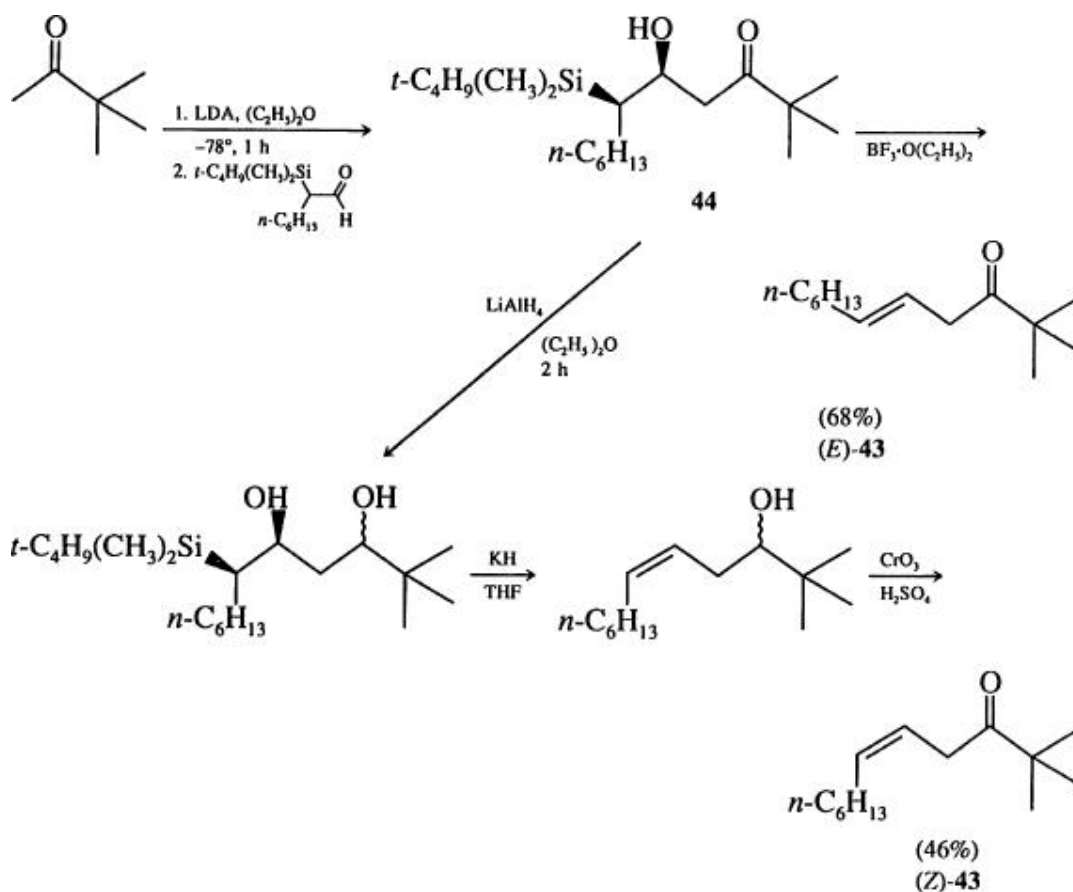
It is noteworthy that addition of ethyllithium to trimethylvinylsilane (**39**) and condensation of the resultant anion with butyraldehyde is diastereoselective, providing a 72:28 mixture of the *threo* and *erythro* isomers of the alcohol **38**. This isomer ratio is evident from subsequent acid- or base-catalyzed elimination.

In addition to hydride, other nucleophiles can be added to α -silylcarbonyl compounds in a diastereoselective manner. (**55**) Reaction of the α -silyl ketone **40** with methyl lithium affords the adduct **41** which, upon treatment with potassium *tert*-butoxide to effect elimination, affords the alkene (*E*)-**42**. Acid treatment of the intermediate **41** yields the isomeric alkene (*Z*)-**42**. (**56**, **57**)

A further example is provided by an aldol method for the preparation of

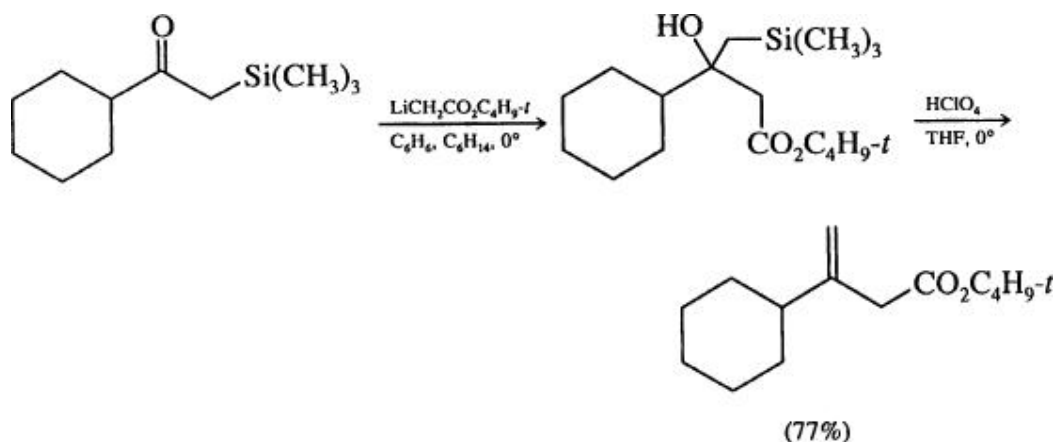


either the (E) - or (Z) - β, γ -unsaturated ketone 43 from hydroxy ketone 44. The reduction–oxidation procedure is necessary to avoid the formation of retro-aldol products during the base-catalyzed elimination. (58)

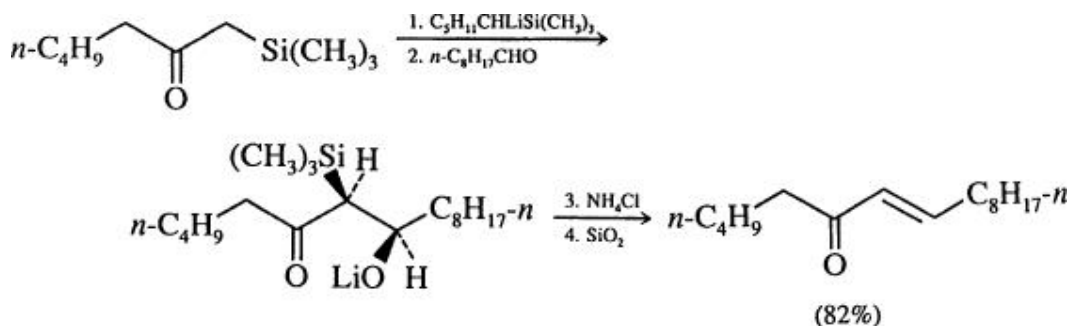


In contrast, attempted condensation of the boron enolate, derived in turn from a trimethylsilyl enol ether, with α -silyl aldehydes fails to give the α -hydroxysilane, the aldol product. (59)

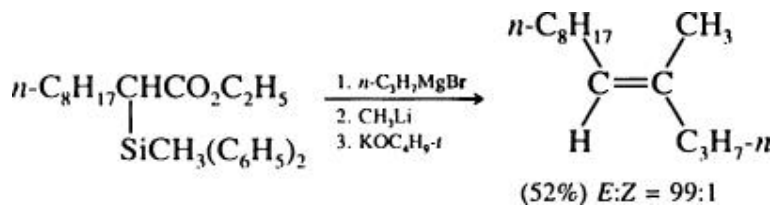
Functionalized carbanions condense in the expected manner with α -silyl ketones. This method can be used to make the thermodynamically less stable β , γ -unsaturated ester isomers. (60)



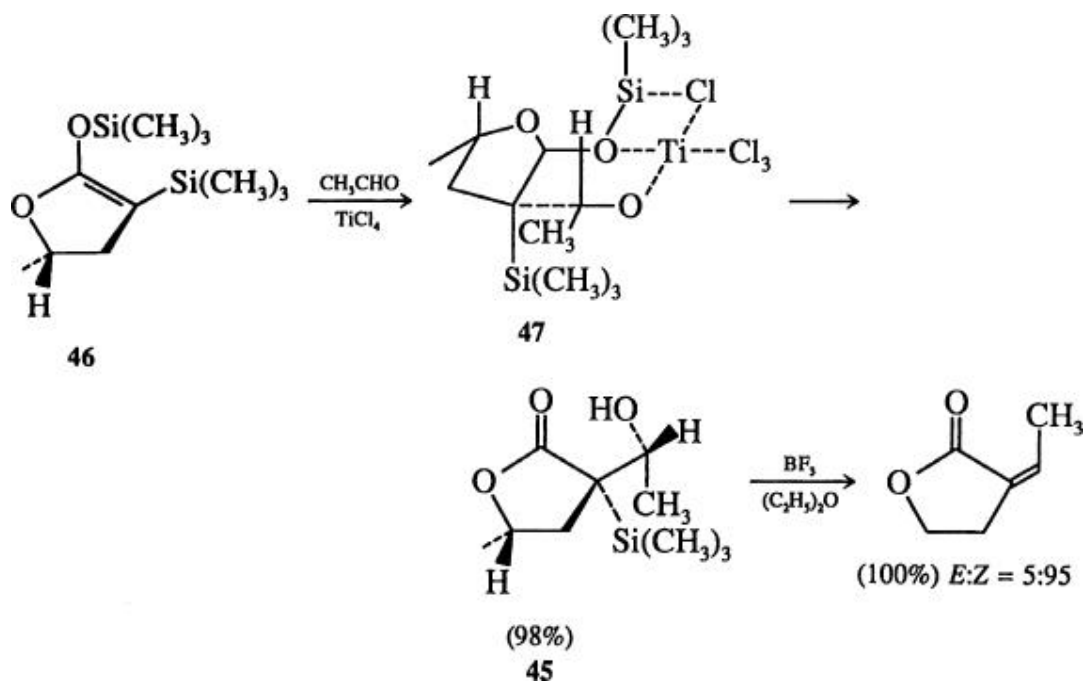
α -Silyl ketones are preferentially deprotonated adjacent to the silyl group by an α -silyl carbanion acting as a hindered base. Subsequent condensation of the enolate with an aldehyde results in the formation of a single enone isomer. (61)



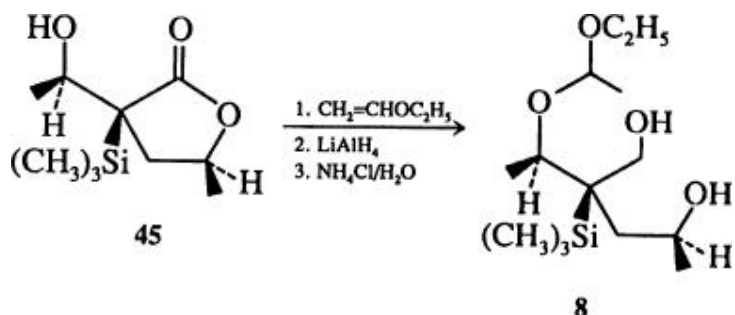
Alkenes are also available from the reaction of hydride donors (62) and organometallic reagents with α -silyl esters. (63)



The Lewis acid silyl enol ether variation of the aldol reaction provides the β -hydroxysilane **45** from the lactone silyl enol ether **46** through the preferred six-membered transition state **47**. (**47**) Subsequent protection of the hydroxy group and reduction with lithium aluminum-hydride provides the β -hydroxysilane



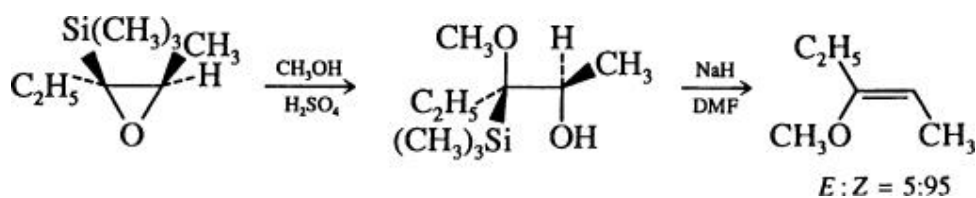
8, whose reactions have already been discussed (Eq. 6). (**34**)



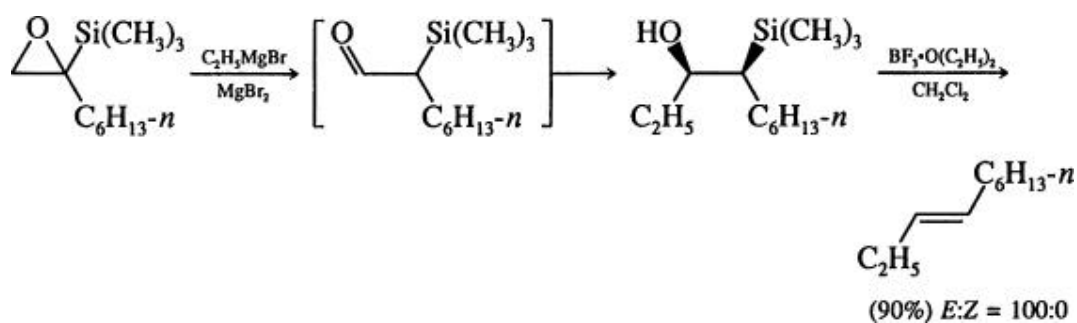
3.1.1.2. From Epoxides and Diols

α , β -Epoxy silanes provide some useful methods for the preparation of β -hydroxysilanes because a nucleophile attacks at the carbon atom bonded to silicon under conditions of electrophilic catalysis. (30, 35, 59, 64-71)

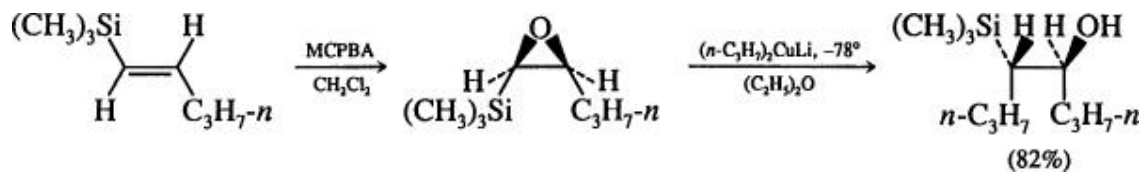
Reaction of an α , β -epoxysilane with a Grignard reagent brings about a rearrangement to produce an α -silyl carbonyl compound which then reacts



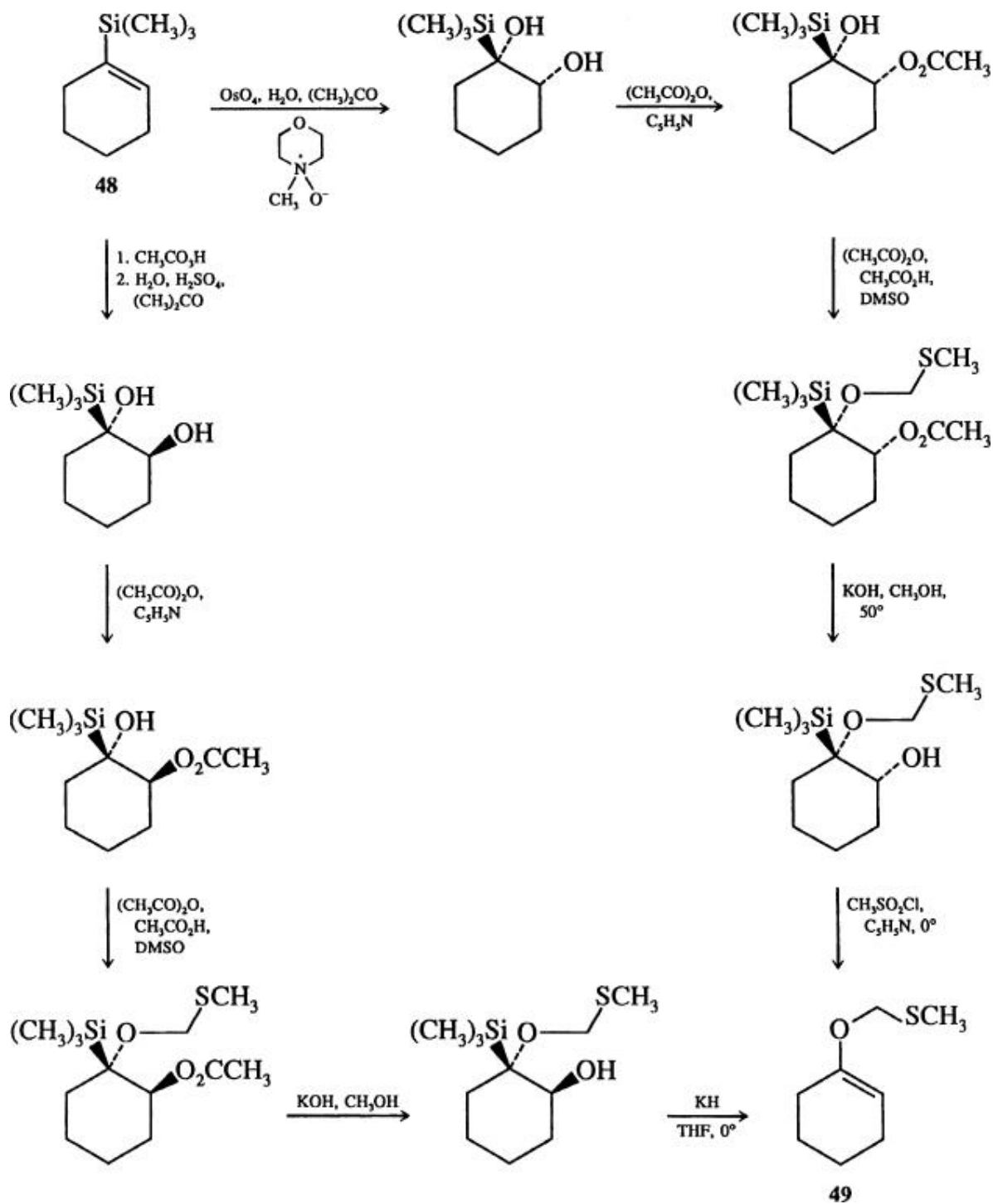
with the organometallic reagent to form predominantly the *erythro* β -hydroxysilane. (72)



Condensation of an α , β -epoxysilane with an organocuprate results in the regio- and stereoselective formation of β -hydroxysilanes. (73)

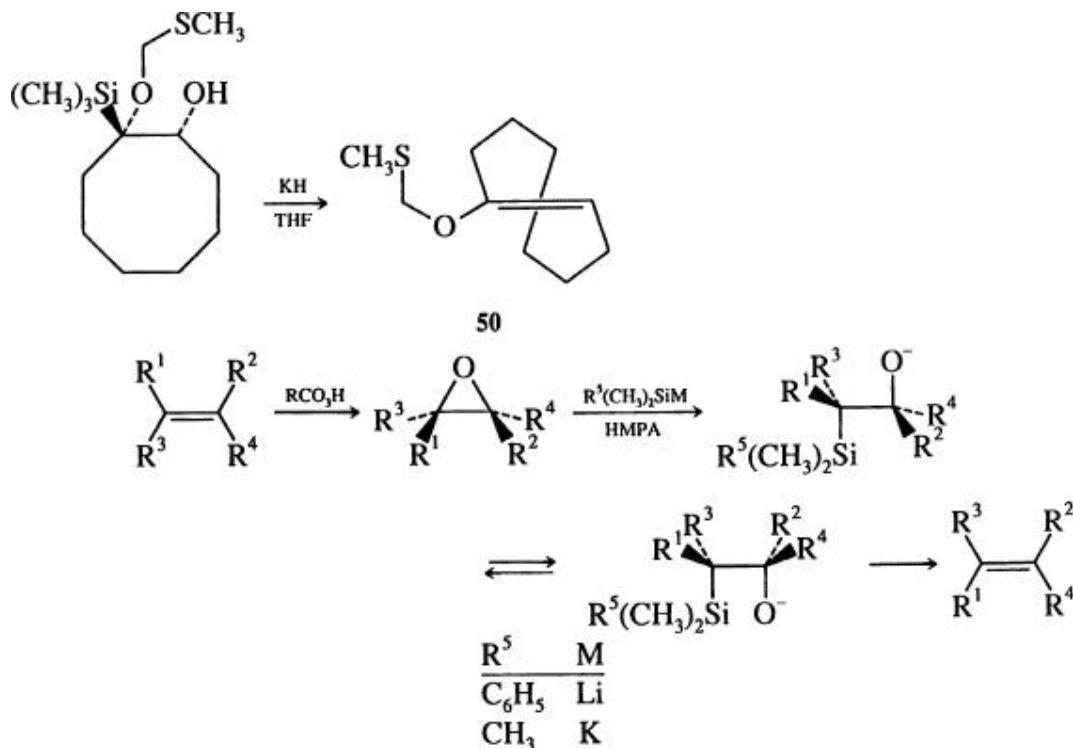


Oxidation of the vinylsilane **48** provides two alternative methods for the preparation of the cyclohexanone enol ether **49**. This methodology can be extended to the preparation of the unstable cyclooctene derivative **50**. (74)



The stereospecific elimination of the Peterson olefination reaction provides two useful synthetic methods for the inversion of alkenes. (75) Both methods rely on the stereospecific opening of an epoxide by a silyl alkali–metal reagent. (30, 76) Although a mixture of regio- and diastereoisomers is formed in the initial

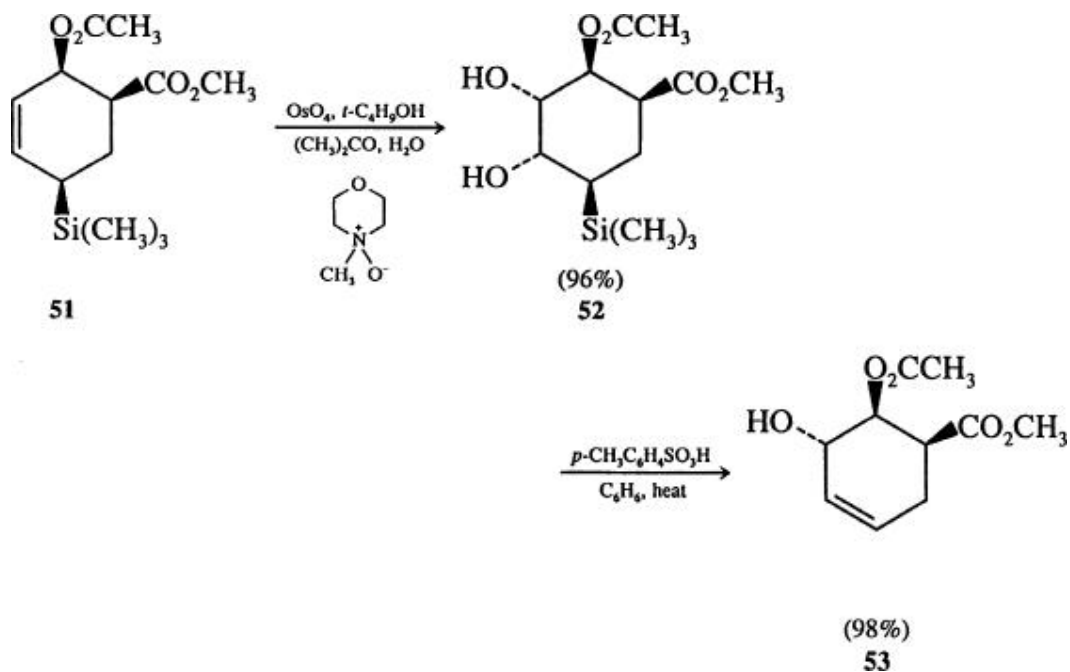
condensation step, the inversion at this center and subsequent *syn* elimination ensure stereospecificity. (77, 78)



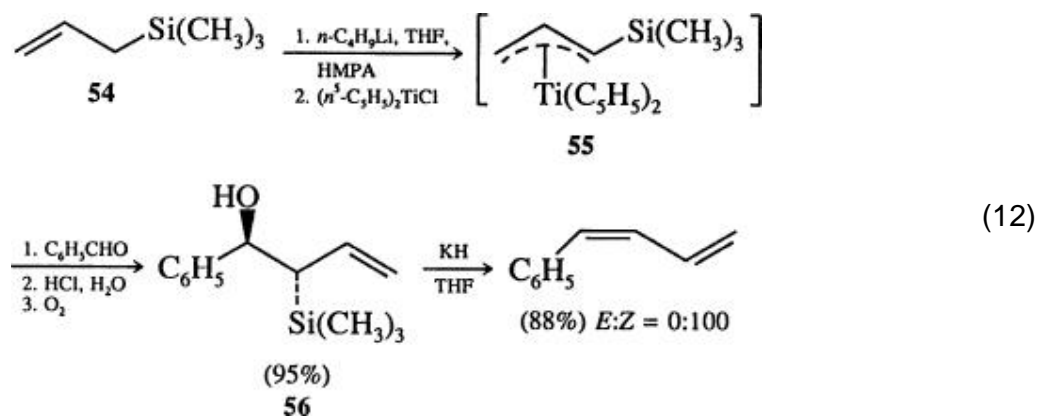
Oxidation of the allylsilane **51** yields the diol **52** stereoselectively. Elimination by an acid catalyst affords the allyl alcohol **53**. (79)

3.1.1.3. From Unsaturated Silanes

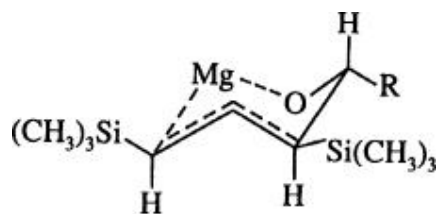
Applications of Cram's rule have made significant contributions to the stereoselective synthesis of β -hydroxysilanes, particularly for the preparation of functionalized silanes. Deprotonation of allyltrimethylsilane (**54**) with *n*-butyllithium, followed by treatment with di- η^5 -cyclopentadienyltitanium(III) chloride results in the formation of the complex



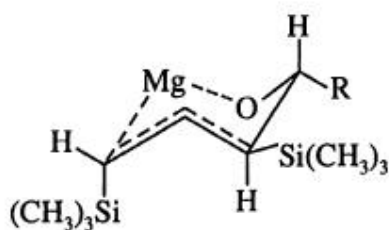
(55). This complex reacts with aldehydes to provide the β -hydroxysilane **56** stereospecifically after acid treatment and air oxidation. The product **56** can be transformed into the (*E*)- or (*Z*)-diene by use of the appropriate acidic or basic elimination conditions. (80, 81)



Similar selectivity is observed with a magnesium counterion for an analogous system (Eq. 5). (28) The stereoselectivity in this case may be attributed to the preferential formation of the transition state **57** over **58**.

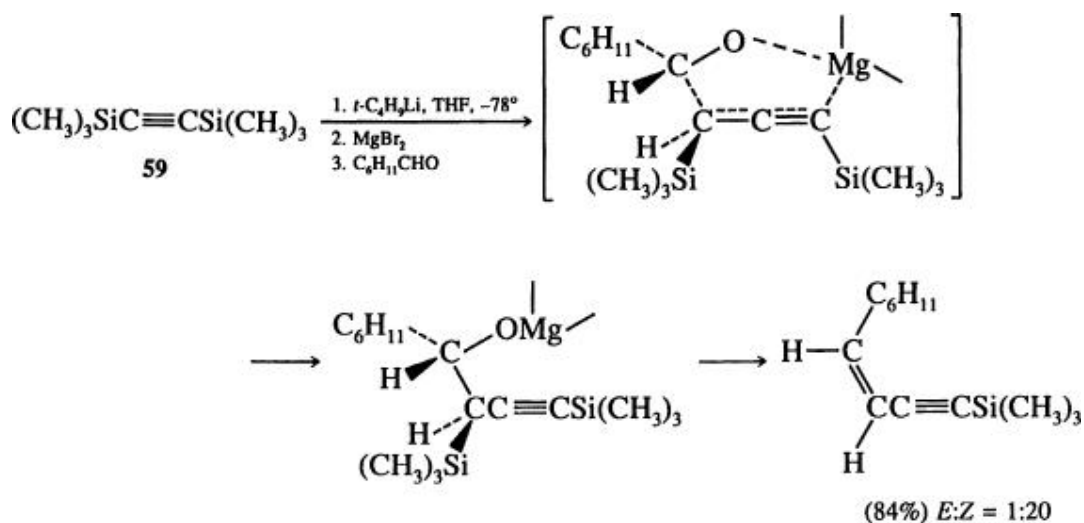


57



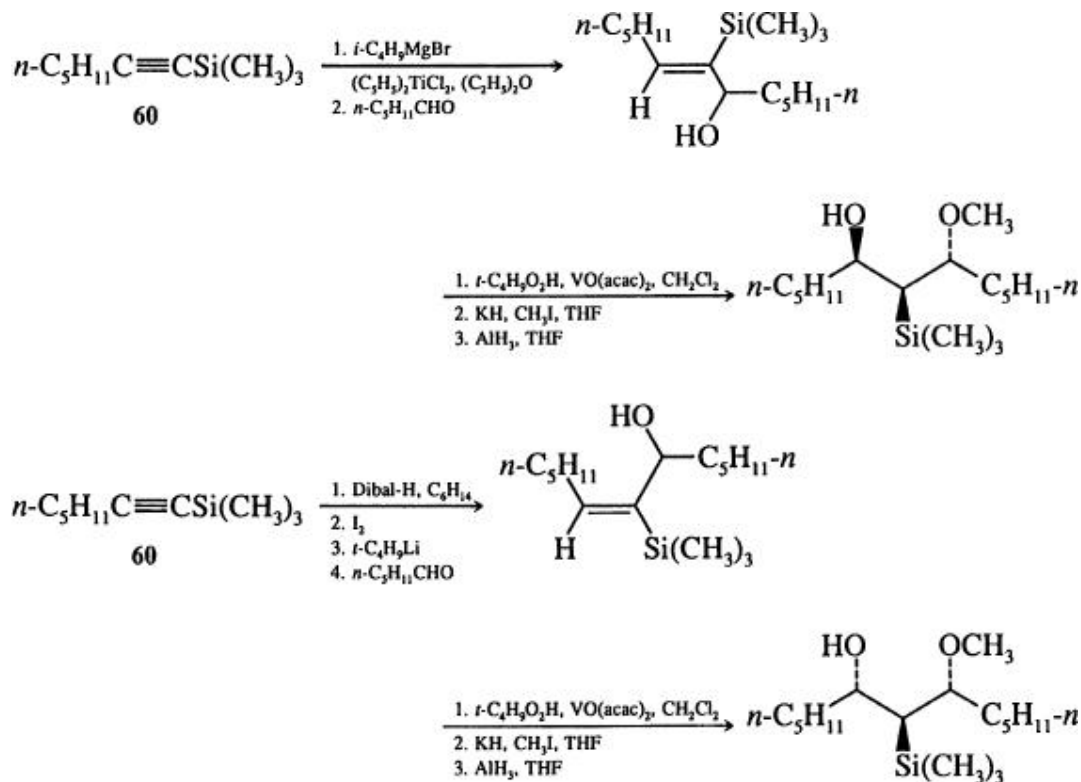
58

A cyclic transition state provides the regioselectivity for the anion derived from 1,3-bis(trimethylsilyl)propyne (**59**). (82)



Stereoselective control of the addition of the anion to carbonyl compounds can arise from the system itself as in cyclic compounds (**83**) or from heteroatom control when it is adjacent to the carbonyl group. (**48-50**, **84**)

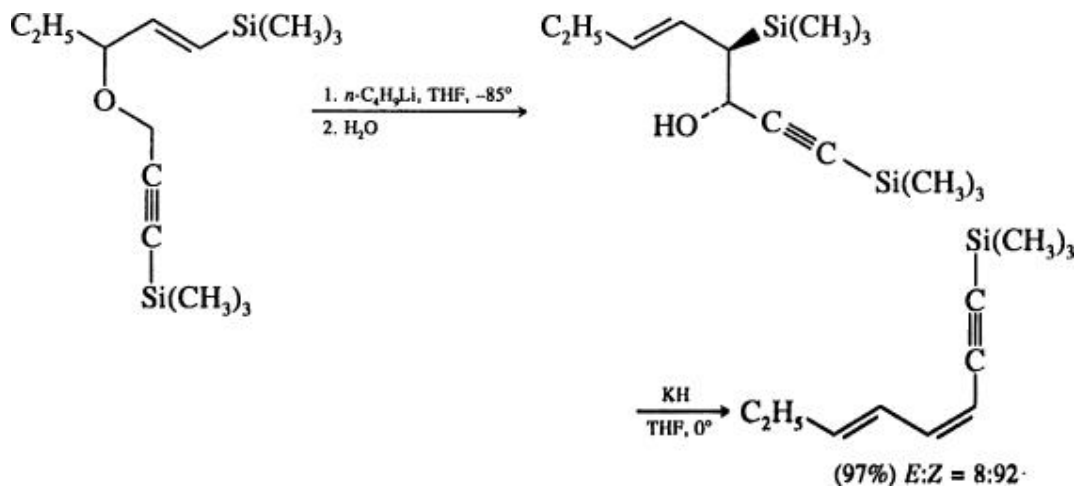
Stereoselective additions to carbon-carbon multiple bonds, as in the acetylene **60**, provide β -hydroxysilanes with various relative stereochemistries. (**36**)



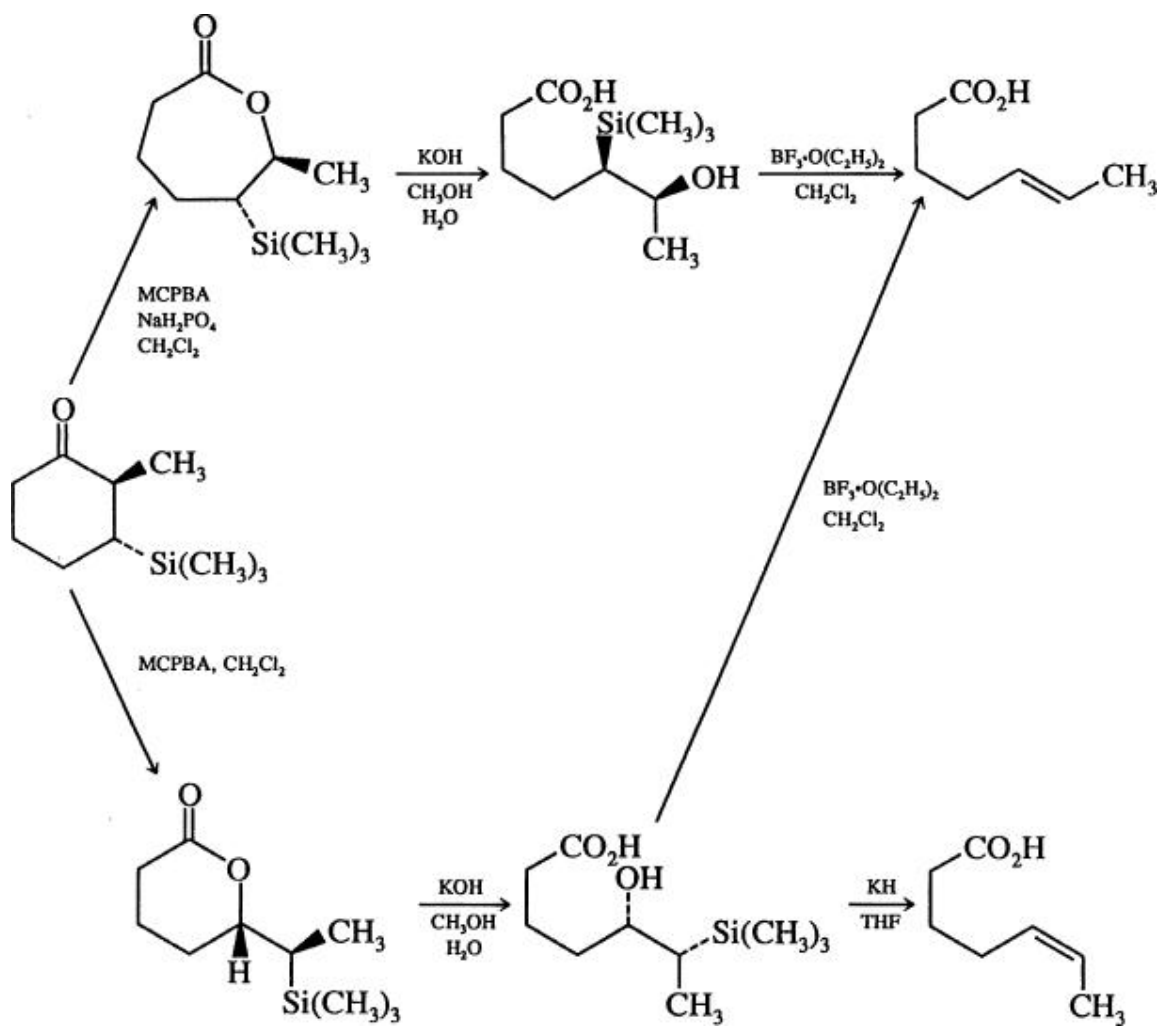
acac = $\text{CH}_3\text{C}(\text{O}^-)=\text{CHCOCH}_3$

3.1.1.4. Miscellaneous Methods

Many stereoselective reactions provide the opportunity for the synthesis of β -hydroxysilanes. One such example is the [2,3]-Wittig rearrangement. (85)



Another such reaction is the Baeyer–Villiger oxidation of γ -ketosilanes with *m*-chloroperoxybenzoic acid (MCPBA) followed by hydrolysis of the lactone. (86)



3.2. Preparation of α -Silyl Carbanions

In the α -silyl carbanions are discussed. Each section considers one type of functional group, or heteroatom, on the same carbon atom as the silyl moiety. In certain cases, additional examples with remote functionality are included when that functional group influences the outcome of a reaction. The preparation and reactions of α -silyl carbanions have been reviewed previously. (21, 87, 88)

3.2.1. Alkyl and Aryl Substituents

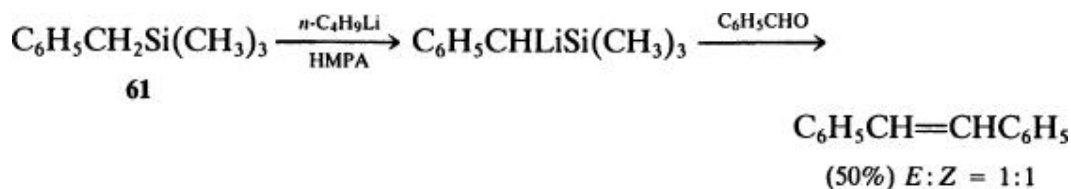
3.2.1.1. Direct Deprotonation

The simplest method for the preparation of an α -silyl carbanion is the direct deprotonation of the parent silane by a base. Unfortunately, this procedure is only generally applicable when an electron-withdrawing group is also present to stabilize the resultant carbanion.

Although silicon does stabilize an α -carbanion, (89) it does not have a marked effect on the kinetic rate of deprotonation. Treatment of tetramethylsilane with *n*-butyllithium—*N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex in hexane gives, after 4 days, a 36% yield of the α -silyl carbanion as detected by subsequent reaction with an electrophile. The analogous reaction with *n*-butyltrimethylsilane gives about the same degree of deprotonation. (90)

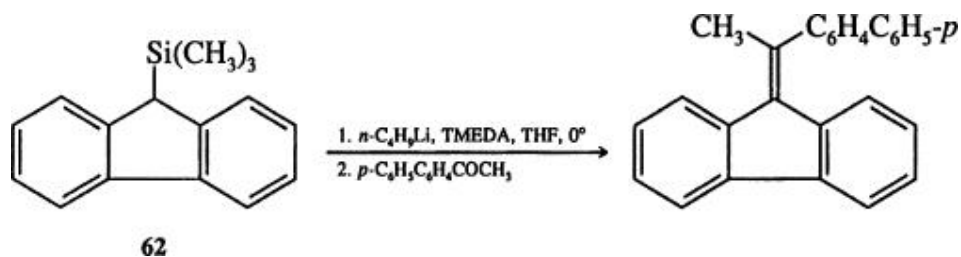


Direct deprotonation in the alkyl series is not a viable method for the preparation of the requisite metalated derivative. However, arylsilanes can be directly deprotonated in good yield under strongly basic conditions. For example, benzyltrimethylsilane (61) is deprotonated by *n*-butyllithium in hexamethylphosphortriamide (HMPA). (91, 92) An analog of the silane 61, benzyltriphenylsilane, provides additional stabilization to the carbanion owing to

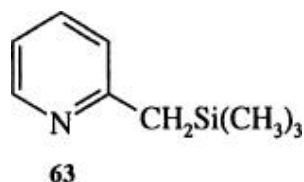


the aryl groups on silicon, and deprotonation is achieved by *n*-butyllithium in ether. (93) Stabilization of the anionic species by two aryl groups as in 62 also

facilitates the deprotonation. (94) This approach is useful for the preparation of sulfines (Eq. 28, p. 73). An example is known where a functionalized silyl moiety [$(t\text{-C}_4\text{H}_9)_2\text{BrSi}$] does not interfere with the deprotonation. (95)

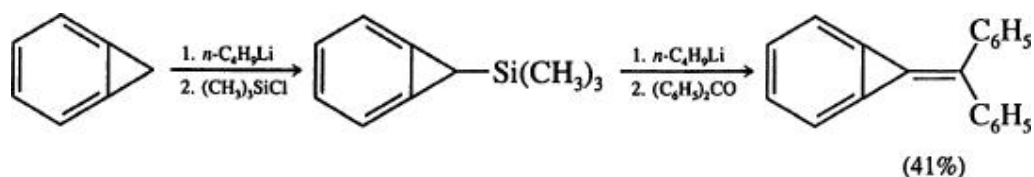


The pyridine analog **63** is deprotonated by the relatively mild base lithium diisopropylamide



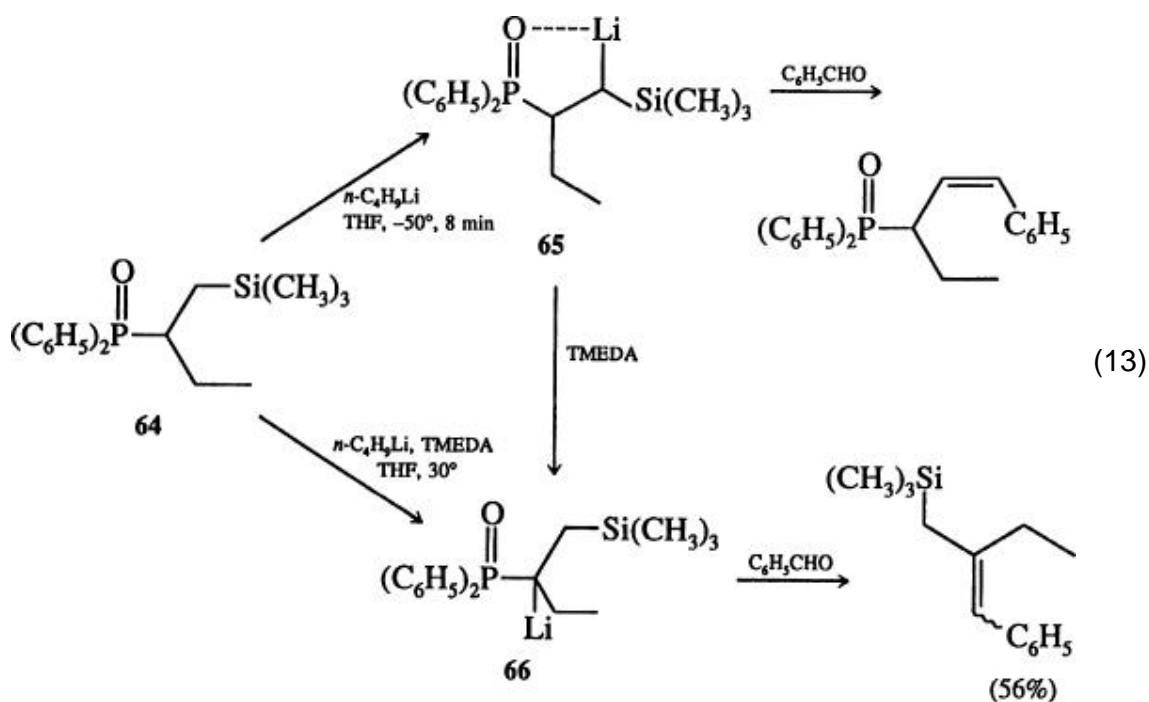
(LDA). (96) The nitrogen atom is probably playing a significant role through complex formation and this example is, therefore, discussed in detail with nitrogen-containing α -silyl carbanions.

The ability of an aryl group to stabilize an adjacent carbanion allows a one-pot procedure to be performed for the introduction of the silyl moiety and the subsequent condensation with a carbonyl compound. (97)

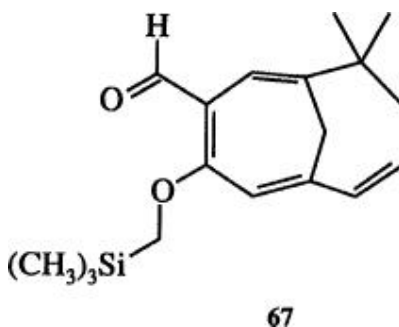


On occasion, the acidity of protons adjacent to a silyl group can be enhanced by a neighboring group. Thus, silane **64** is deprotonated by *n*-butyllithium in tetrahydrofuran (THF) at -50° within 8 minutes, as detected by further reaction of the carbanion. (98) The silyl group increases the kinetic acidity of the α -methylene group since unsubstituted diphenyl-*tert*-butylphosphine oxide is

very difficult to deprotonate. The addition of TMEDA to the organolithium **65**, or reaction of the parent silane **64** with base in the presence of this complexing agent, affords the anion adjacent to the phosphorus group **66**. Treatment of this anion **66** with benzaldehyde yields an allylsilane through a Horner–Wittig reaction. (99) The generality of this reaction (Eq. 13) remains to be established. (100)

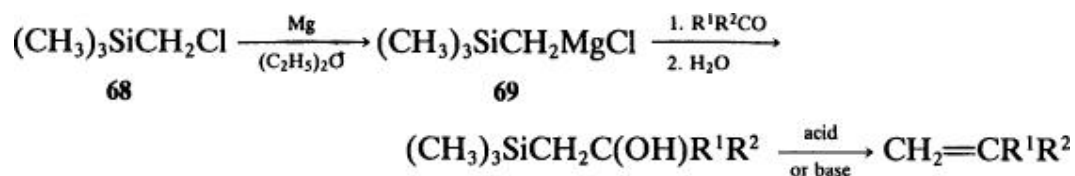


Sometimes the direct deprotonation approach fails. Even the use of strong bases with **67** does not effect an intramolecular Peterson reaction. (101)



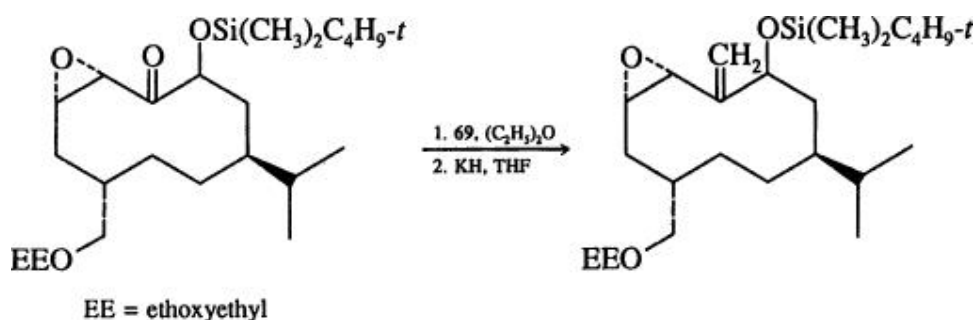
3.2.1.1.2. Formation of Grignard Reagents

α -Halosilanes are converted into the corresponding Grignard reagents by classical techniques. (102) Because of trimethylsilylmethyl chloride's (68) availability, (21) trimethylsilylmethylmagnesium chloride (69) is by far the most commonly used reagent in this class. Grignard reagent 69 is useful for methylenations and provides an alternative

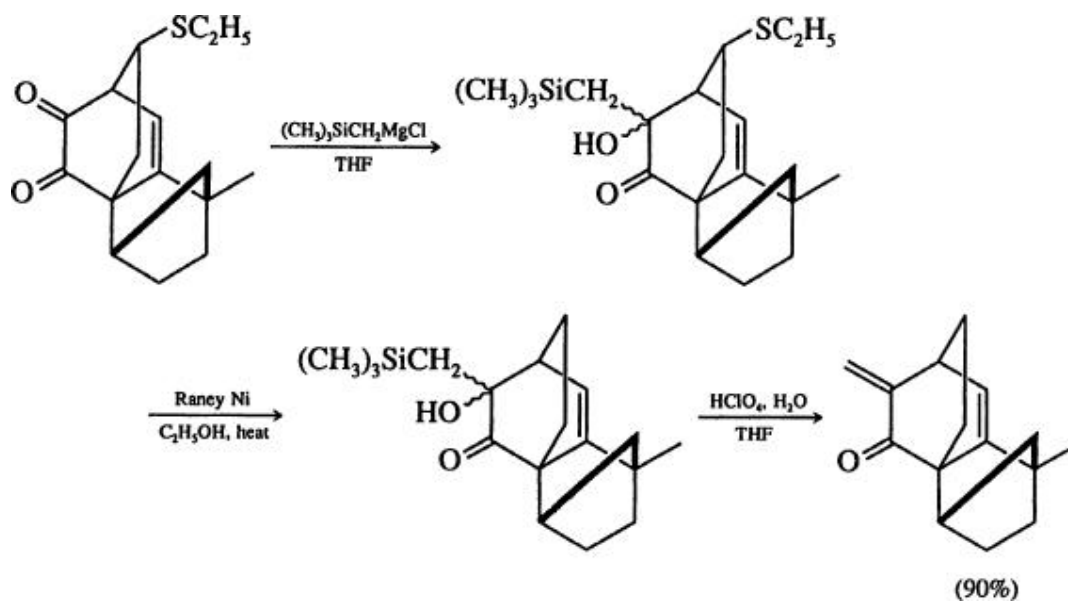


to the classic Wittig reagents. (103-108) Since the metal counterion is magnesium, the intermediate β -hydroxysilane can be isolated. (91, 92) Unfortunately, higher homologs of the α -halosilane 68 are often tedious or troublesome to prepare. (109)

An example of the use of the Grignard reagent 69 for methylenation is provided as part of a synthesis of periplanone-B, the sex excitant pheromone of the American cockroach. (110)



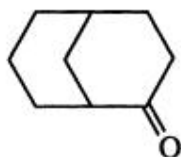
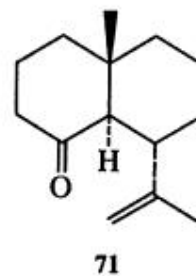
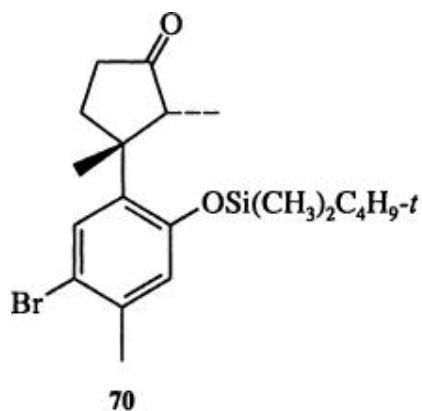
The ability to isolate the β -hydroxysilane has been used to effect a stereoselective reduction in an approach to a substituted denudatine system. (111, 112)



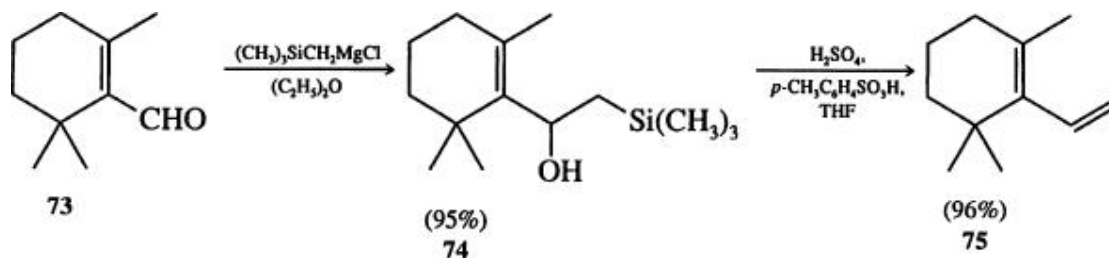
The Grignard reagent **69** is sterically demanding and does not add to hindered ketones, such as **70**, (113-115) but does react with others, such as **71**, when a Wittig reagent fails. (116)

Preferential axial attack (93%) is observed between the α -silyl Grignard reagent **69** and the bicyclic ketone **72**. Forcing conditions (NaH, THF, 150° , 10 hours) must be used to effect elimination. (117)

Condensation of **69** with acrolein results in 1,2 addition, (118, 119) while reaction

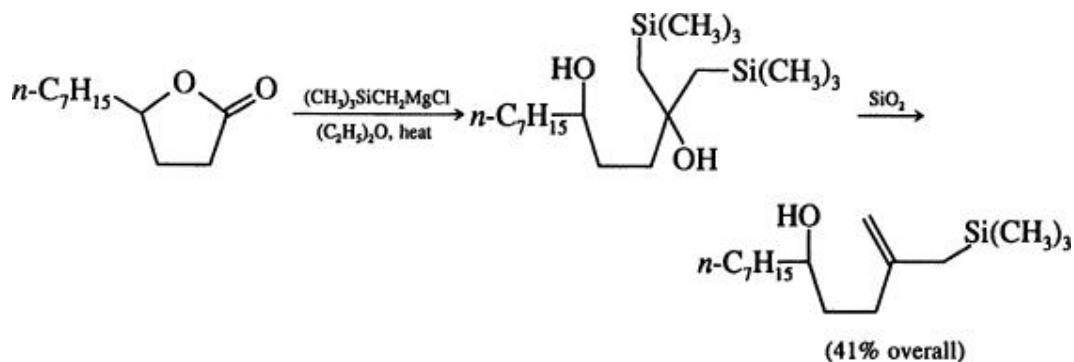


with conjugated ketones favors a 1,4 mode of addition. (120) The enal β -cyclocitral (**73**) reacts in a 1,2 manner to yield the β -hydroxysilane **74**. Subsequent treatment of **74** with sulfuric acid in the presence of *p*-toluenesulfonic acid affords the pure diene **75**. (121) In contrast, reaction of the silane **74** with sulfuric acid alone, or with potassium hydride in tetrahydrofuran, results



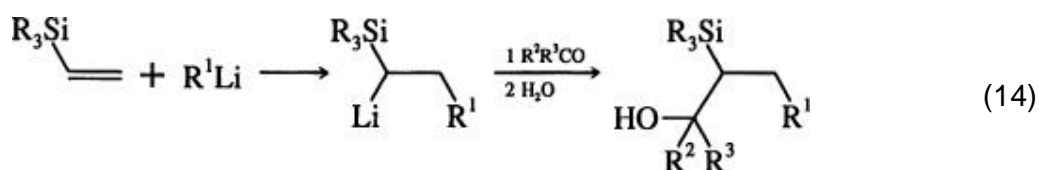
in significant amounts of the silyl diene, indicating that dehydration is a significant competing reaction pathway in this system. (122)

Reaction of the Grignard reagent **69** with esters substituted adjacent to the carbonyl group leads to α -silyl ketones; (123) these latter compounds can then react with a second equivalent of **69** if the steric requirements are not too overpowering. (100) In a similar manner, reaction of a lactone with excess reagent **69** provides an ω -hydroxyallylsilane. (124)



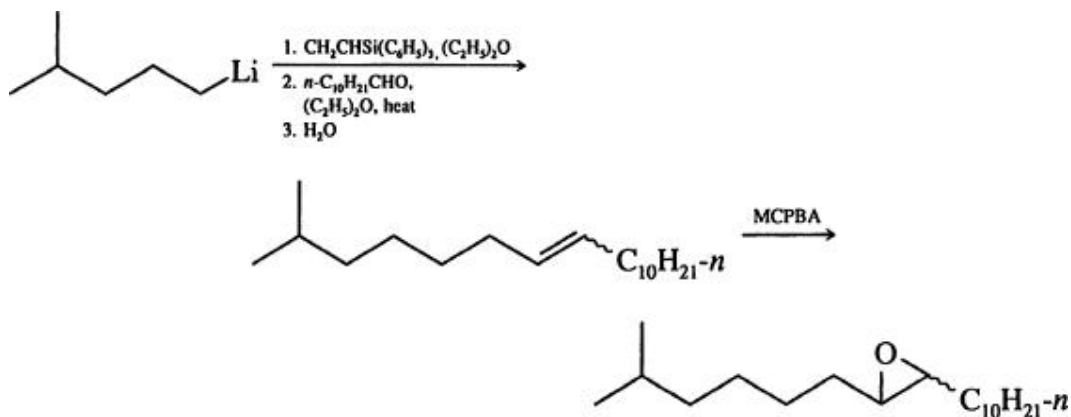
3.2.1.1.3. From Vinylsilanes

Alkylolithiums add to vinylsilanes regioselectively to provide α -silyl carbanions, (125, 126) which can then react with a carbonyl compound. The addition is clean with simple vinylsilanes, (26) particularly if the

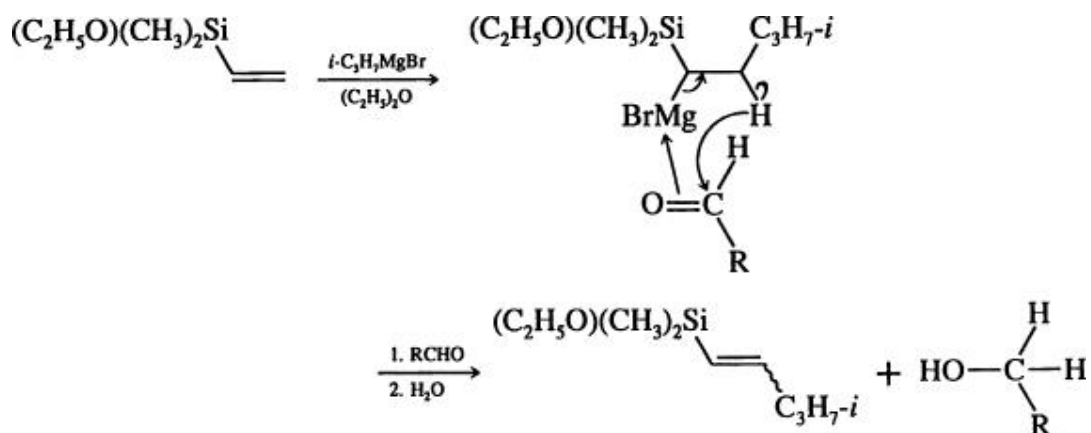


silyl group is triphenylsilyl (Eq. 14, R = C₆H₅). (91-93, 127) The addition is susceptible to steric effects in the alkylolithium and at both alkene termini. (128) The methodology provides a route to the sex pheromone of the gypsy moth (Disparlure). (91)

Grignard reagents do not add to vinylsilanes unless electron-donating

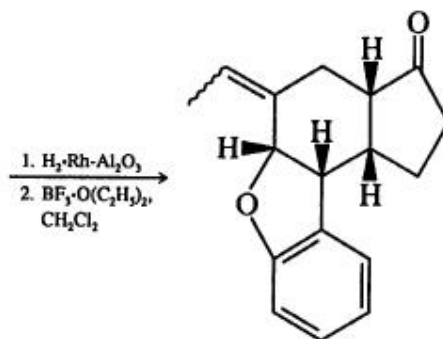
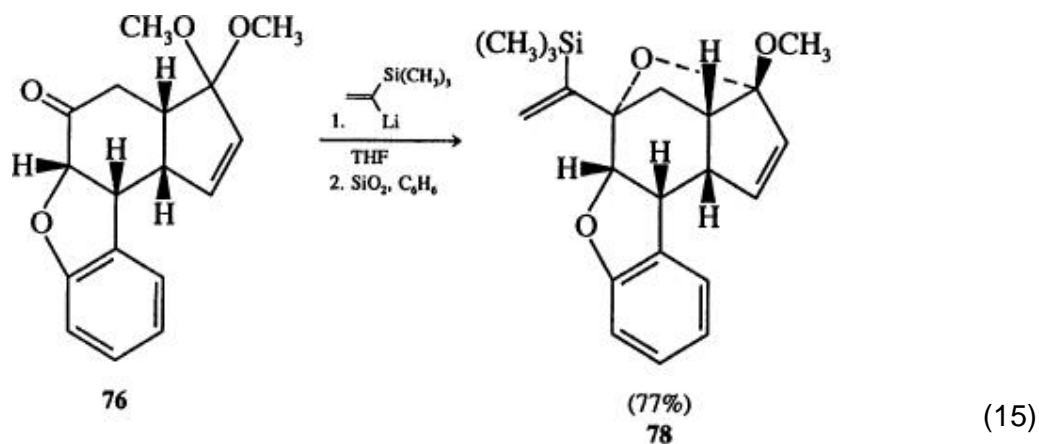


groups are present in the silyl moiety. (129, 130) Subsequent addition of a carbonyl group to the Grignard adduct results in reduction of the carbonyl group to give an alcohol. (91)

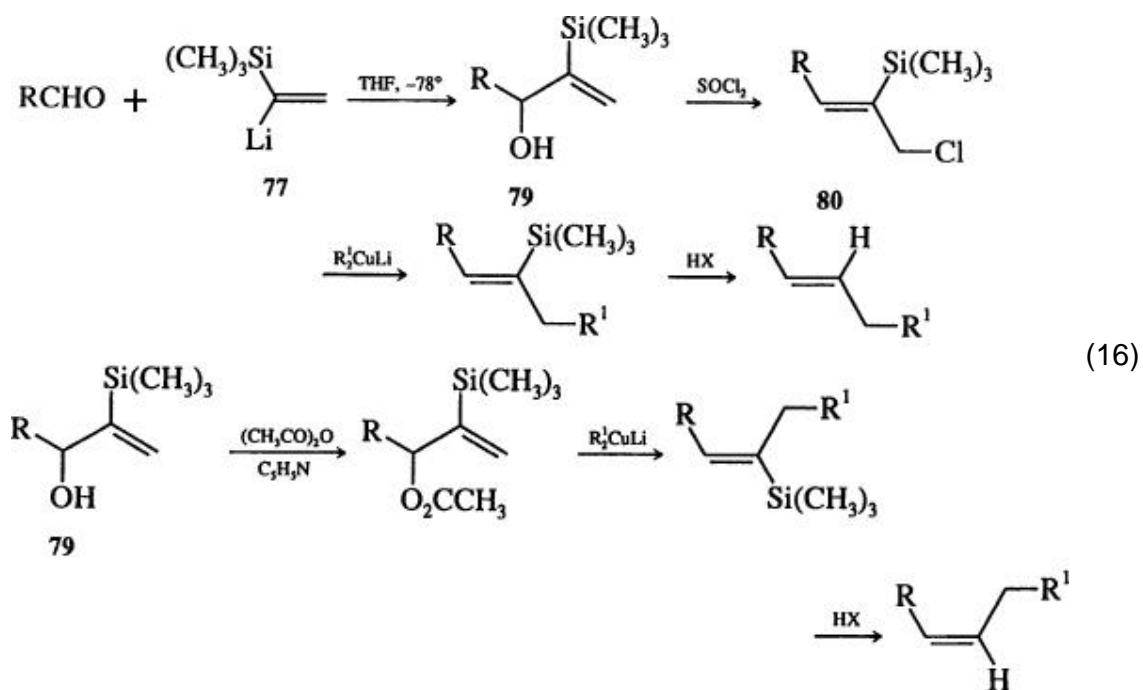


Vinylsilanes contain an alkene functional group in addition to the silyl moiety. This unsaturation can be used to prepare functionalized alkenes such as allenes (Eq. 17, p. 36). Vinylsilanes can, however, provide useful routes to alkenes based on α -metallovinylsilanes. (131-133)

In some cases the Peterson olefination reaction may lead to an alkene when a Wittig reaction fails because of enolization of the carbonyl compound caused by the basic phosphorus ylide. While neither ethylenetriphenylphosphorane nor 1-(trimethylsilyl)ethylmagnesium chloride forms an addition compound with the ketone **76**, the use of α -trimethylsilylvinyl lithium (**77**) circumvents this problem and provides the ketal **78** after acid-catalyzed cyclization. The alkene is unmasked by Lewis acid treatment. (83) An alternative approach,



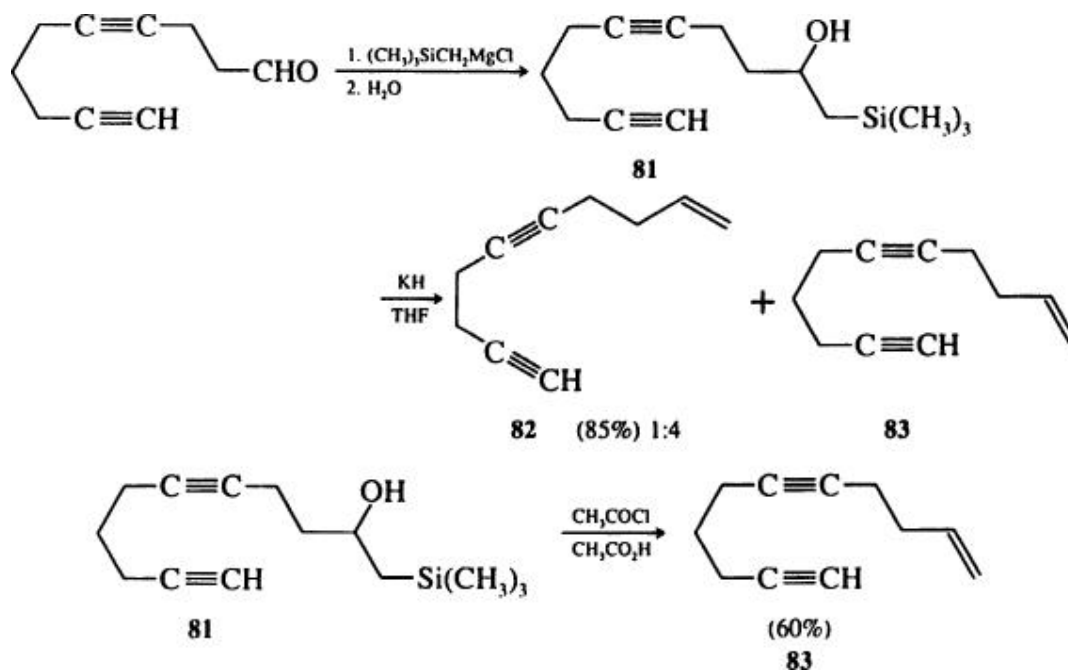
which allows variation in the alkene substitution pattern, relies upon the condensation of the vinyl lithium reagent **77** with aldehydes through the intermediary of **79** and **80**. (134-136)



This method has been elaborated to prepare α -silylenones for use in an annelation procedure. (137)

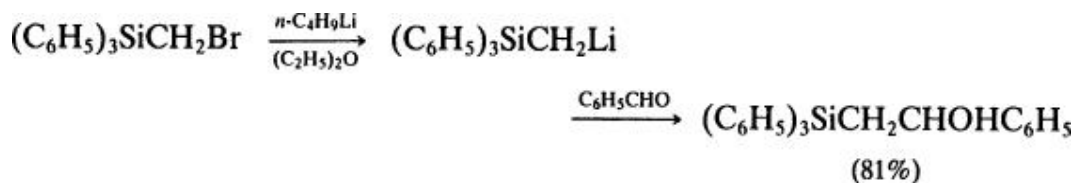
The acetylation procedure (Eq. 16) provides an alternative method for the formation of alkenes from β -hydroxysilanes by way of the vinylsilane. (138, 139) The silane **81** is stable to hydrochloric acid, while use of potassium hydride results in the formation of the base-catalyzed isomerization product **82** in addition to the simple elimination product **83**. In contrast, treatment of the alcohol **81** with acetyl chloride in acetic acid provides **83** as the sole product. (140)

It is possible, however, for β -hydroxysilanes to be esterified—for example, with propionic anhydride in the presence of triethylamine and 4-(dimethylamino)pyridine (DMAP)—and used in subsequent transformations without elimination occurring. (141)



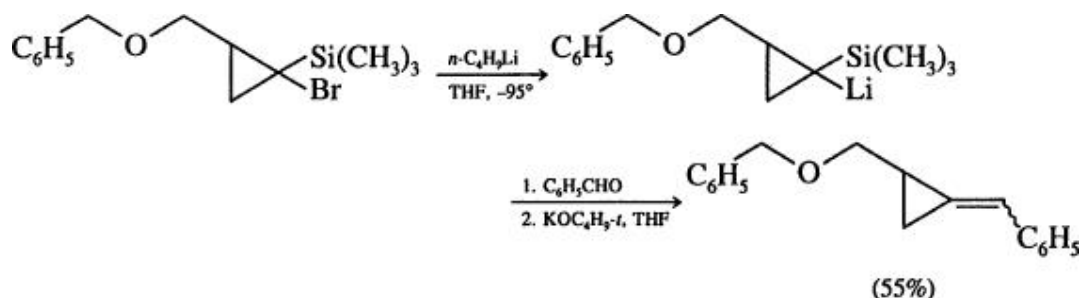
3.2.1.1.4. α -Silylalkyllithiums from Halides

The halogen atom of an α -halosilane can be transmetalated by an alkyllithium. (21, 93) The methodology provides a



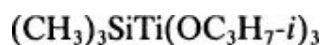
useful route to α -silyl carbanions as illustrated by the formation of cyclopropyl derivatives. (142, 143)

Use of lithium metal, rather than an alkyl lithium, also results in the formation of an α -silylalkyllithium from an α -halosilane. (87, 144, 145) As with the Grignard approach, the general availability of α -halosilanes, other than the simple



ones such as those derived from benzylsilanes, (109, 146) seriously curtails the utility of this displacement method. Thus various functional groups or heteroatoms can be used in place of the halogen to facilitate both introduction of the silyl moiety and a transmetalation reaction.

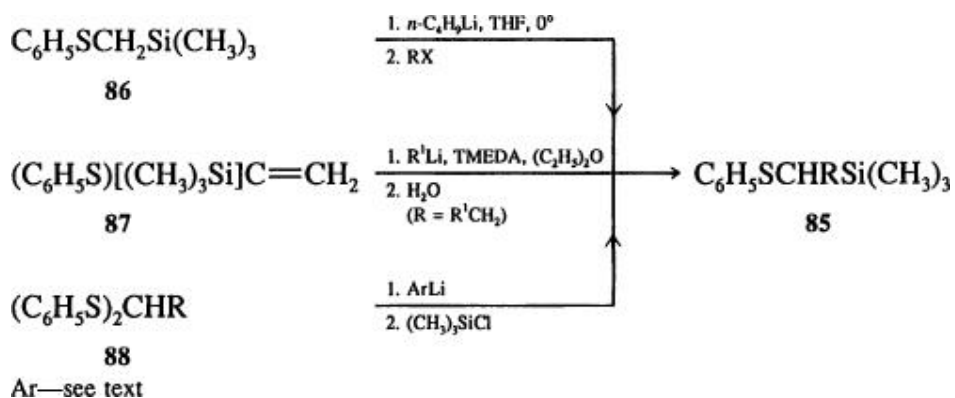
The reactions of α -silylalkyllithium reagents are very similar to those described for the analogous Grignard reagent. The use of the titanium reagent **84**, formed from the corresponding alkyl lithium, has been advocated to minimize proton abstraction reactions. (147)



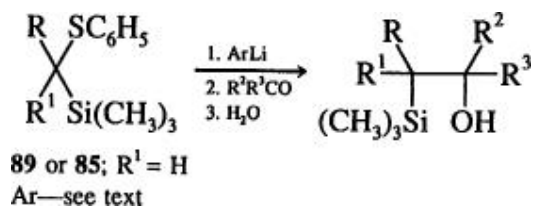
84

3.2.1.1.5. α -Silylalkyllithiums from Sulfides

A sulfide provides a wide variety of approaches for the introduction of the silyl group and the subsequent formation of the α -silyl carbanion. The required α -silylsilane **85** is obtained by alkylation of the anion of phenylthiotrimethylsilylmethane (**86**), (148-150) by addition of an alkyl lithium to the alkene **87**, (151-153) or by silylation of the lithio derivative obtained from a bis(phenylthio)acetal **88**. (153-155) The latter two methods also can be used for the preparation of dialkyl analogs **89**.



The replacement of the phenylthio group by a lithium atom is accomplished with a variety of reagents which include lithium naphthalenide (154, 156, 157) and lithium 1-(dimethylamino)naphthalenide. (155) The latter reagent has the advantage that the aryl byproduct, 1-(dimethylamino)naphthalene, can be easily

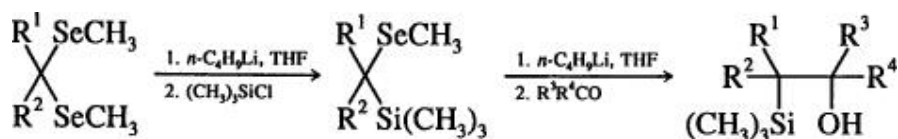


separated from the desired product. (158) In contrast, lithium naphthalenide is prepared from readily available, inexpensive precursors. (159, 160) In many cases, separation of the naphthalene byproduct is not difficult; (157) it is not, however, always trivial. (136, 161, 162) Other reagents that have been used to effect reductive lithiation of sulfides are lithium di-*tert*-butylbiphenyl (163) and tri-*n*-butylstannyl lithium. (164)

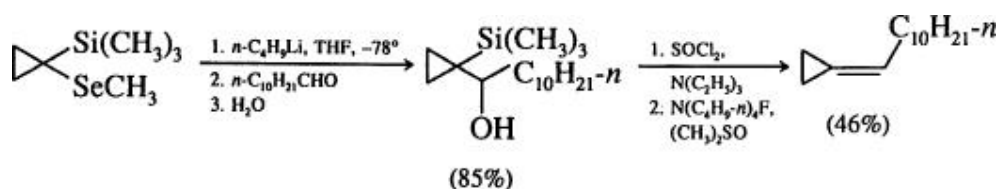
The elimination of the β -hydroxysilane can be accomplished by a one-pot reaction sequence through careful choice of workup conditions. (157)

3.2.1.1.6. α -Silylalkyllithiums from Selenides

A selenium group may be exchanged for lithium by treatment of the selenide with an alkyllithium. (165) Thus a one-pot sequence for the introduction of the silyl group and subsequent carbanion formation is a straightforward procedure.

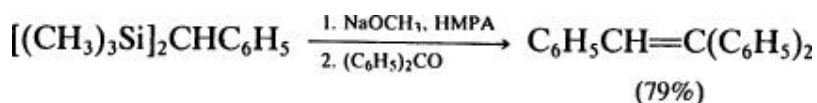


Cyclopropylidene derivatives are available by this protocol, although in some cases elimination from the β -hydroxysilane with potassium is not clean. The required transformation is accomplished by thionyl chloride followed by fluoride ion. (147)

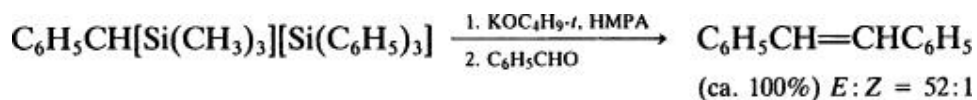


3.2.1.1.7. α -Silylalkyllithiums from Silanes

Silicon itself can be displaced from a bis(silane) to provide an α -silyl carbanion. An alkali metal alkoxide in the polar solvent HMPA is required to achieve this transformation. (166) If two different silyl groups are present, the less sterically hindered group is preferentially

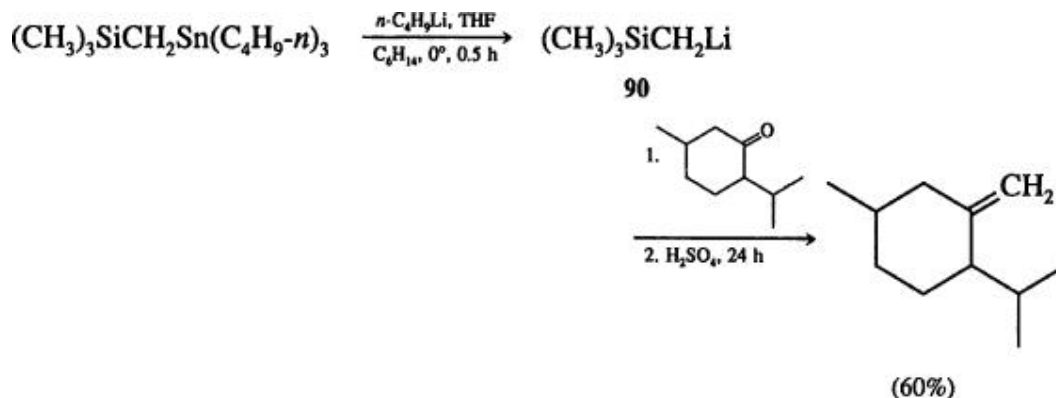


cleaved. (37)



3.2.1.1.8. α -Silylalkyllithiums from Stannanes

In a manner very similar to that used for selenides, stannanes are readily transmetalated by alkylolithiums. The approach provides a useful method for the preparation of trimethylsilylmethylolithium (90), (167) which, in addition to reacting with aldehydes and ketones, reacts with carboxylic acids, esters, and acid chlorides to give α -trimethylsilyl



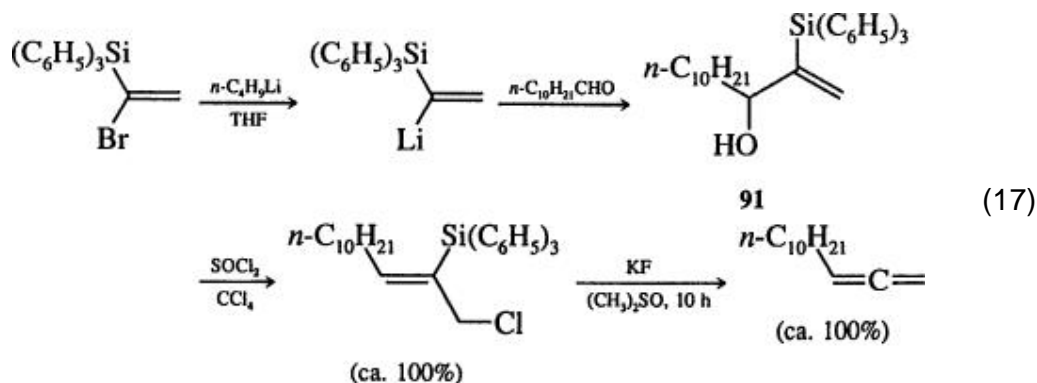
ketones in good yields. (123, 168)

3.2.2. Preparation of α -Silyl Carbanions Containing Unsaturation (169)

3.2.2.1.1. From Vinylsilanes

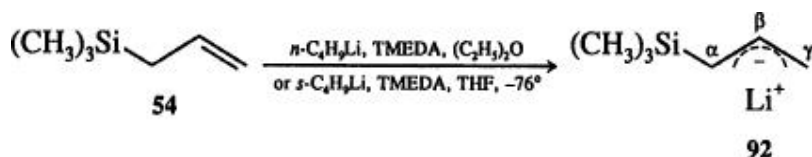
α -Lithiovinylsilanes are readily available by metalhalogen exchange, and react with a wide variety of electrophiles including aldehydes and ketones (Eq. 16). (132, 133, 136, 137, 170) The analogous Grignard reagents are also available.

The allyl alcohols **91** (cf. **79**) are resistant to the conditions usually employed for the elimination of β -hydroxysilanes. The allene is prepared by treatment of the alcohol **91** with thionyl chloride to give the rearranged allyl chloride (cf. **80**), which is then followed by fluoride ion in dimethyl sulfoxide. (171, 172)

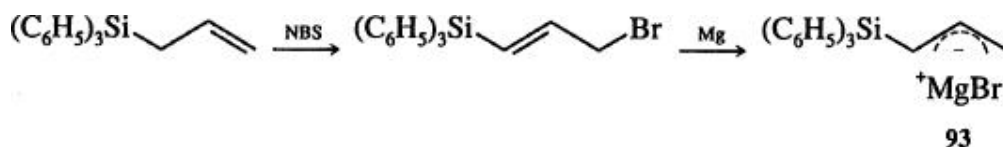


3.2.2.1.2. From Allylsilanes

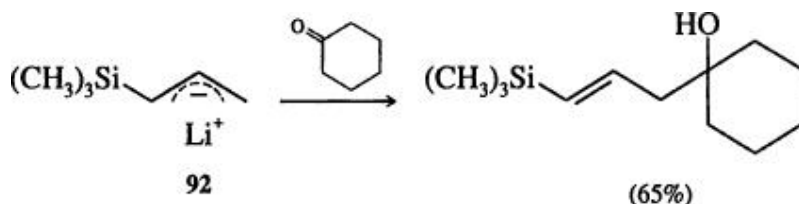
In these cases, an allyl anion is prepared and, as a consequence, it is more stable than the vinyl anions just described. Allyltrimethylsilane (**54**) is deprotonated by *n*-butyllithium–TMEDA complex in ether, (173) or by *sec*-butyllithium–TMEDA in tetrahydrofuran. (174) An analogous



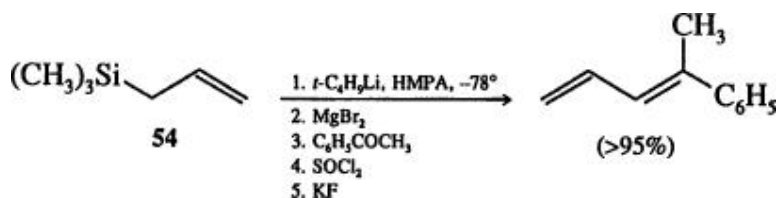
Grignard reagent is available from the bromide. (175)



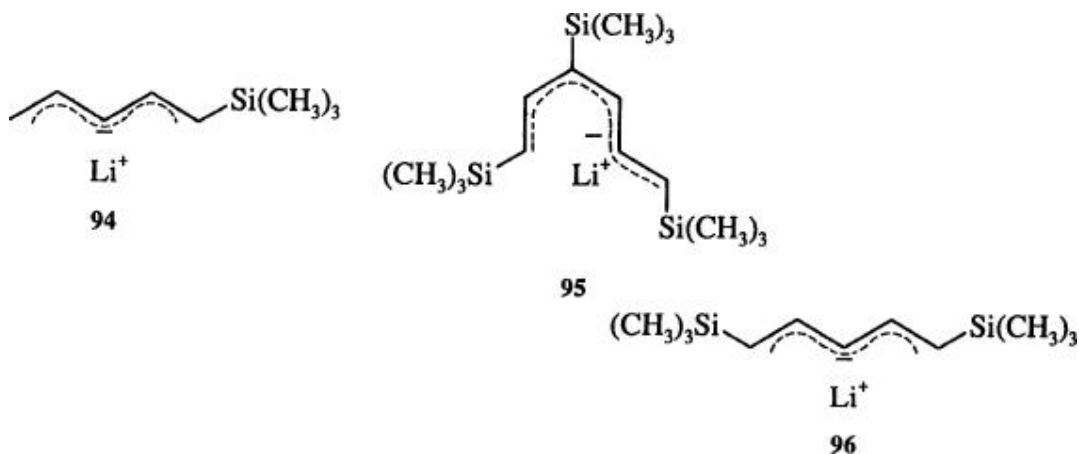
Ambident anions **92** and **93** react with carbonyl compounds at the γ position and thus the Peterson reaction is not feasible. (174, 175) However, the regioselectivity can be changed by the use of additives, such as magnesium bromide (Eqs. 5 and 12). Elimination in these cases is accomplished by thionyl or



acetyl chloride followed by fluoride ion. (176) Of course, in some cases the allyl anion is symmetrical and the regioselectivity problem does not exist.

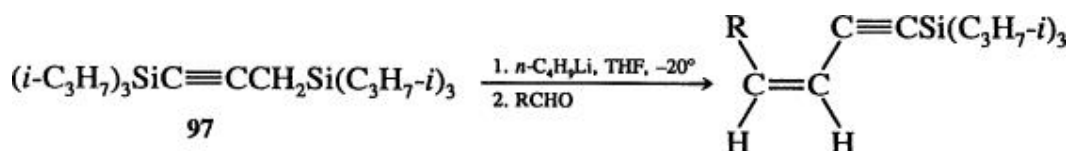


When the degree of conjugation is increased, as in the anion **94**, the principal reaction with a carbonyl compound occurs at the ϵ position. The anions **95** and **96** afford polyenes when condensed with carbonyl compounds since both termini bear silyl groups. (177) Even larger conjugated systems are possible (Eq. 18). (178)



3.2.2.1.3. From Silylacetylenes

Addition of an aldehyde to the lithio derivative of 1,3-bis(trimethylsilyl)propyne (**97**) results in a *cis* enyne. When HMPA is used as cosolvent, the stereoselectivity is changed in favor of the *trans* enyne. This selectivity is rationalized by the allenic anion being the most reactive species in tetrahydrofuran, while the propargylic anion is the predominate species reacting in the presence of HMPA. (179)



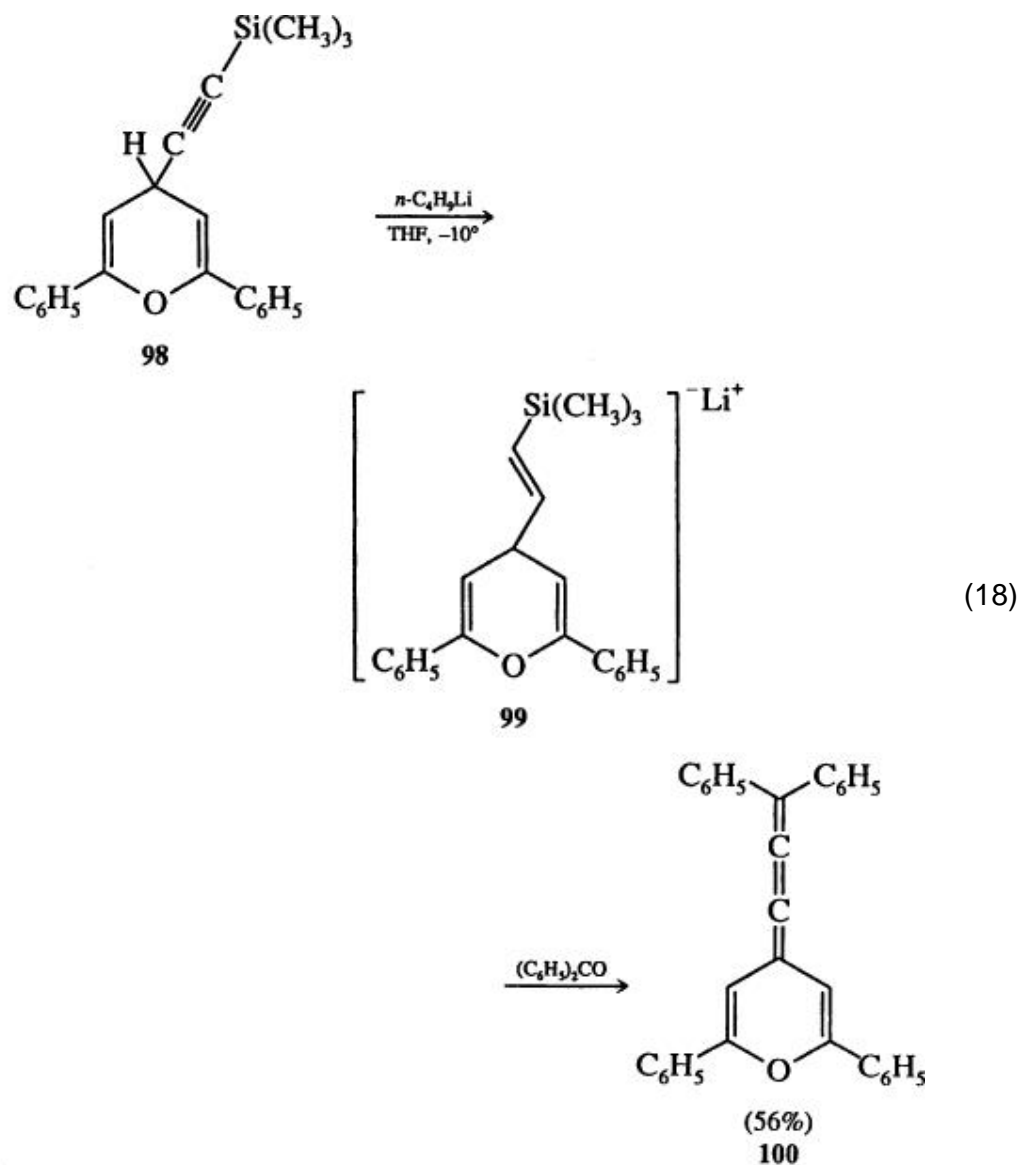
Deprotonation of the Δ^4 -(4*H*-pyranyl)-substituted acetylene **98** results in the highly delocalized anion **99**. This organolithium **99** reacts with carbonyl compounds to provide cumulenes **100**. (180)

3.2.2.2. Preparation of α -Silyl Carbanions Containing Carbonyl Groups

α -Silyl ketones and aldehydes are relatively labile compounds which are desilylated by many nucleophilic and electrophilic reagents. (181) This property, together with the indirect methods that have been used for the preparation of α -silyl ketones such as silylation of the enolate, usually results in reaction at the oxygen center. (13) Thus, α -silylcarbonyl compounds have not found widespread application in the Peterson olefination reaction. Methods that are successful for the synthesis of α -silyl ketones include the addition of a cuprate derived from trimethylsilylmethylmagnesium chloride (**69**) and an acid chloride, (123, 182, 183) isomerization of α , β -epoxysilanes, β -silylallyl alcohols, (184, 185) or a silyl enol ether, (186) and reactions of α -selenosilyl

enol ethers. (187)

An example of the use of α -silyl ketones in synthesis is provided by a route to the macrolide narbonolide. (188)

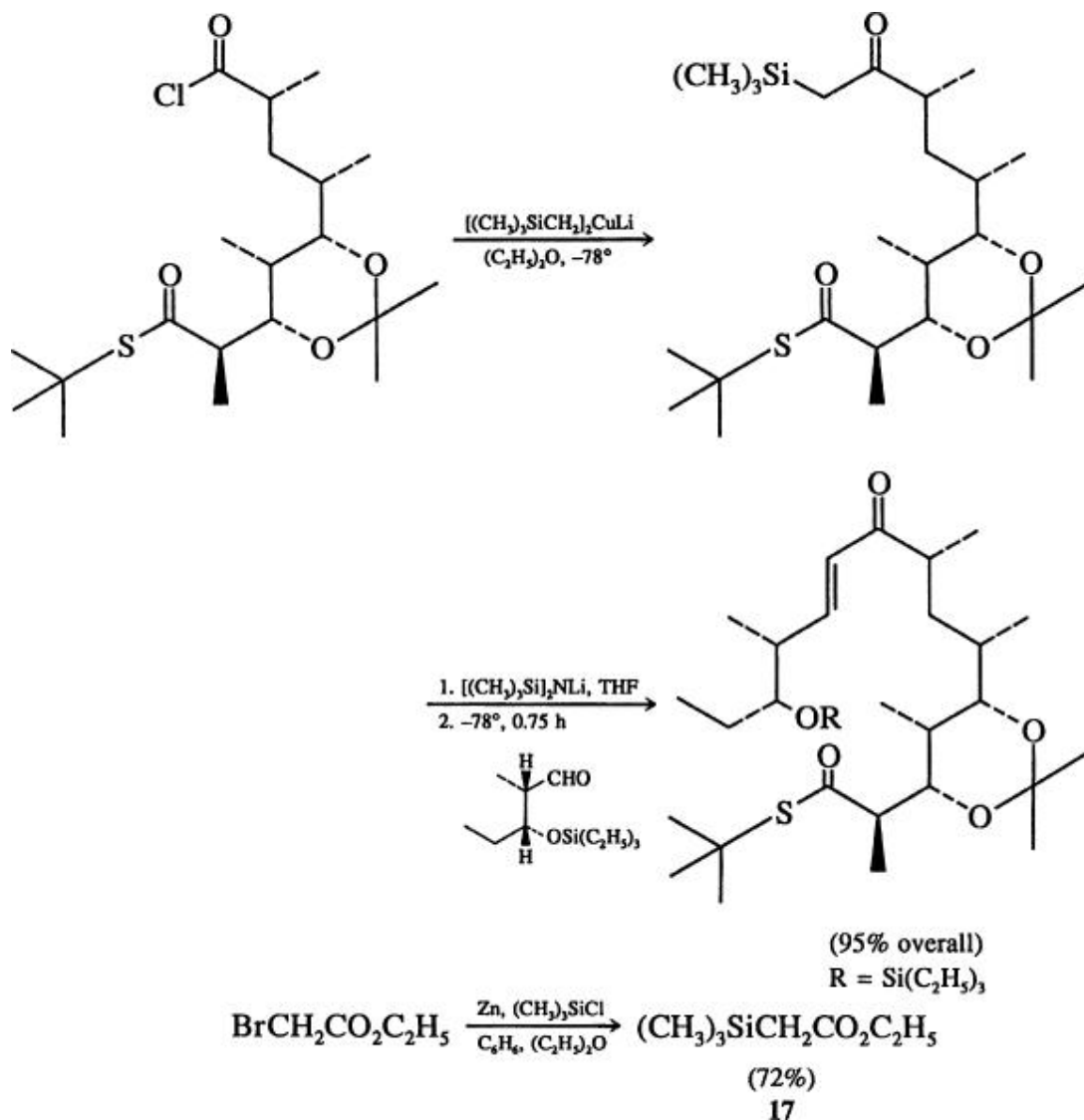


3.2.2.3.1. α -Silyl Esters (189)

Problems associated with α -silyl esters are similar to those with α -silyl ketones—namely, a labile silyl group and a preference for O-silylation of the ester enolate. (190) The routes to α -silyl esters are more direct than those to their ketonic counterparts.

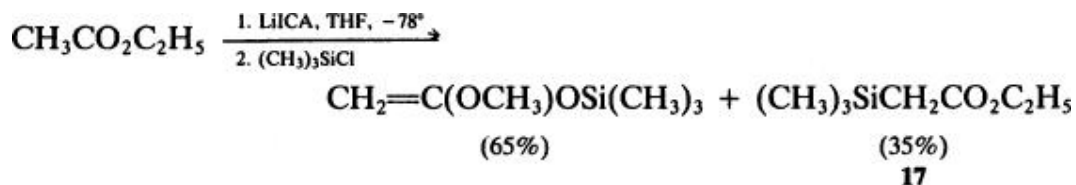
The first synthesis of ethyl trimethylsilylacetate (**17**) resulted from reaction of trimethylsilylmethylmagnesium chloride (**69**) with ethyl chloroformate. (**191**) More general approaches have since been developed.

α -Silyl esters are available from a modified Reformatsky reaction of the α -bromoester with a silyl chloride. (**192**) Low yields are, however, obtained when other α -substituents are present in the ester or if a large, bulky silyl chloride is used.



Silylation of ester enolates, such as that derived from ethyl acetate, results in a mixture of the *O*- and *C*-silylated products. In the presence of HMPA, the

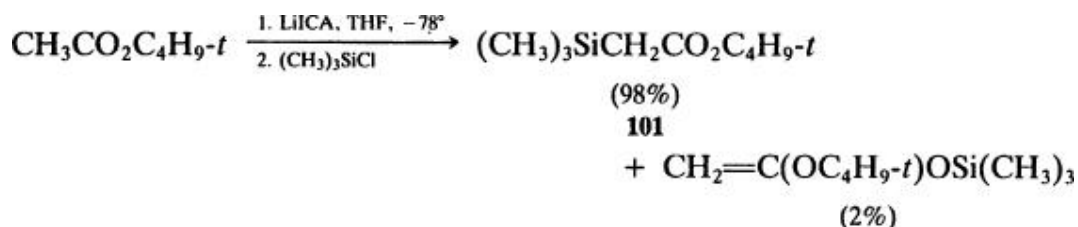
amount of C-silylation is augmented. (193) The degree of O-silylation is increased by the use of higher temperatures (0°) and trimethylsilyl chloride



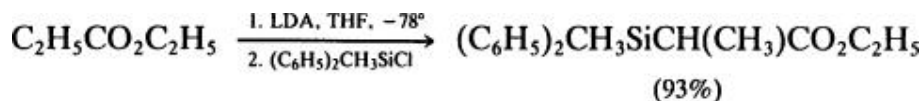
LiICA = lithium *N*-isopropylcyclohexylamide

as electrophile. (194)

When a *tert*-butyl ester is employed, the steric bulk of this alkyl group promotes C-silylation, often to the extent that O-silylation is effectively excluded. (193) Alkylation of the enolate derived from an α-silyl ester allows higher homologs

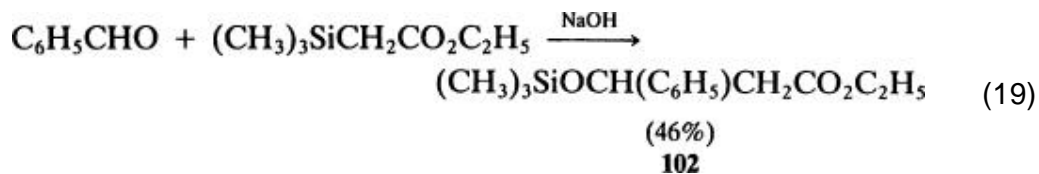


to be prepared. (195) An alternative procedure is provided by silylation of an ester enolate with chlorodiphenylmethylsilane. (196) This regioselectivity can be



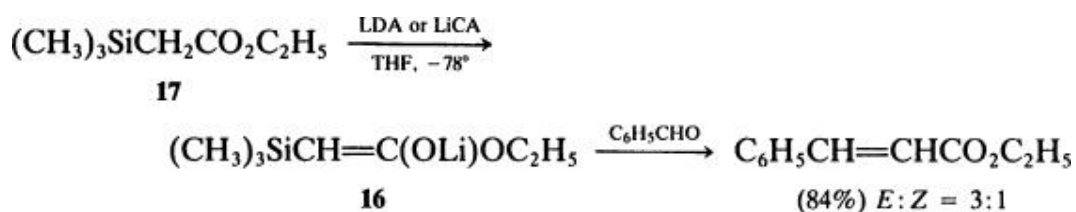
attributed to softer acid characteristics of the silyl chloride rather than steric effects; the addition of HMPA increases the amount of O-silylation.

Condensation of an aldehyde with ethyl trimethylsilylacetate (17) in the presence of a base catalyst leads to formation of 102, the silyl ether of the β-hydroxyester. (197) This ether is eliminated stereoselectively by sodium hexamethyldisilazide. (41)

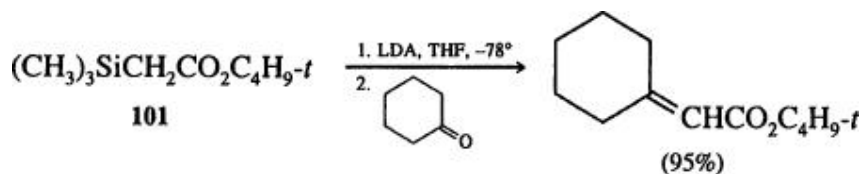


The mechanism of formation of the silyl ether **102**, as shown in Eq. 19, is open to speculation; it could involve desilylation to achieve enolate formation.

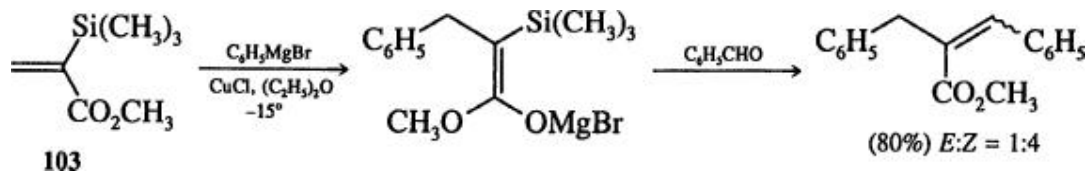
Treatment of ethyl trimethylsilylacetate (**17**) with lithium dicyclohexylamide (LiCA) or lithium diisopropylamide provides the ester enolate **16**, which upon subsequent reaction with aldehydes or ketones, provides the α , β -unsaturated esters directly. (40, 198-200)



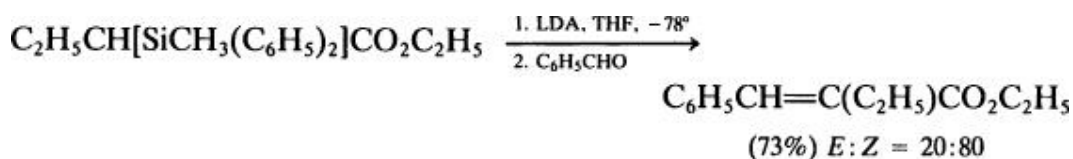
The *tert*-butyl ester **101** reacts in an analogous manner. (201, 202) A variant of this approach, using an acylimidazole in place of a carbonyl compound, provides a route to β -ketoesters. (203)



The enolates of α -silyl esters are also obtained by the copper-catalyzed addition of Grignard reagents to methyl 2-(trimethylsilyl)acrylate (**103**). Subsequent addition of a carbonyl compound results in overall formation of an α , β -unsaturated ester. (204)

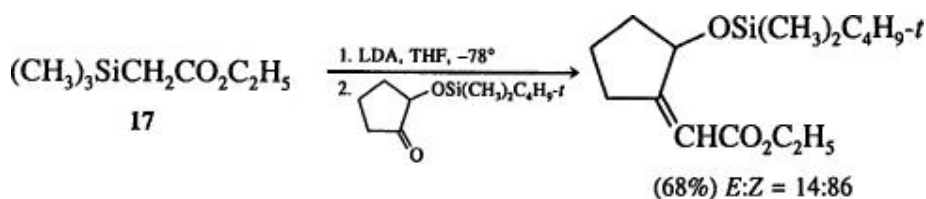


Many of the reactions of α -silyl esters have already been discussed in the context of the stereochemical outcome of the Peterson olefination reaction. Rather than reiterate, it suffices to say that stereochemical control with this class of compounds can be either small (45, 205) or heavily biased toward the *E* isomer (magnesium counterion), (41) or can form the *Z* isomer preferentially (diphenylmethylsilyl group). (42, 43)

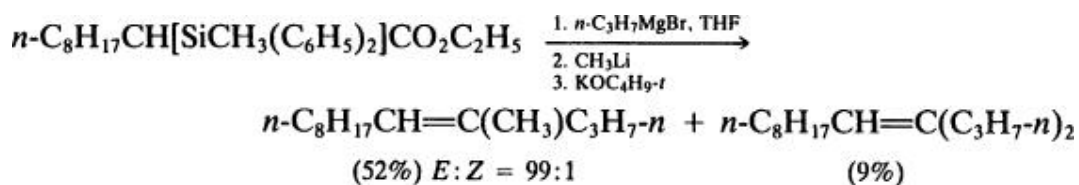


Stereoselective formation of one alkene product is observed when the initial condensation between the α -silyl ester enolate and the carbonyl group is stereochemically controlled, (206) particularly by the presence of heteroatom substituents in the ketonic moiety. (48-50, 84)

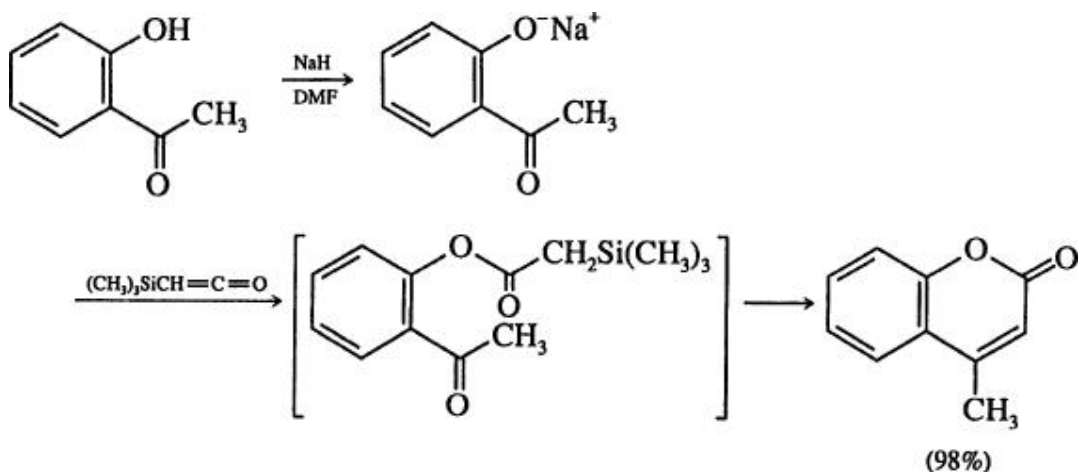
Reaction of the lithium enolate derived from methyl trimethylsilylacetate with 2-cyclopentenone results in 1,4 addition. (207)



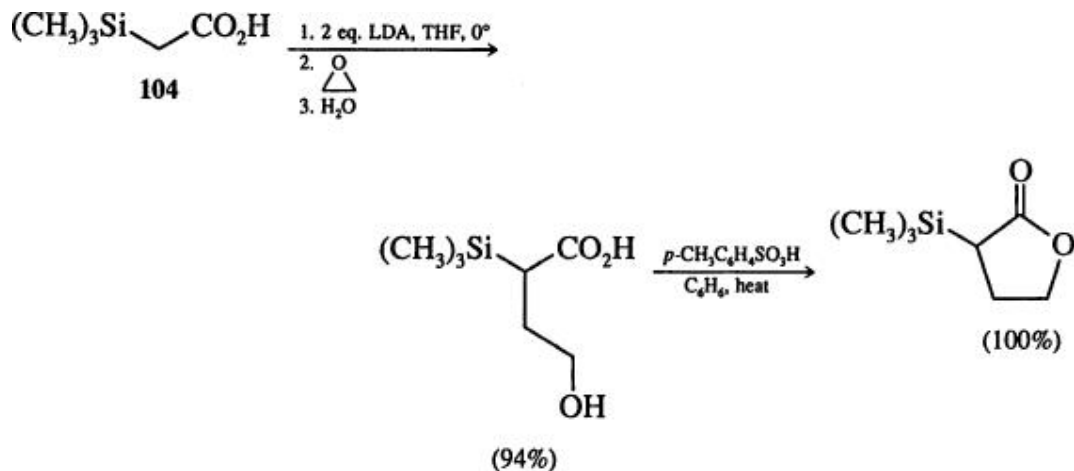
α -Silyl esters provide a useful route for the preparation of alkenes by the Peterson olefination reaction through conversion of the ester moiety to an alcohol by way of a reduction, (62) or reaction with organometallic compounds which undergo Cram addition to the intermediate β -ketosilane. (43, 63, 208-210)



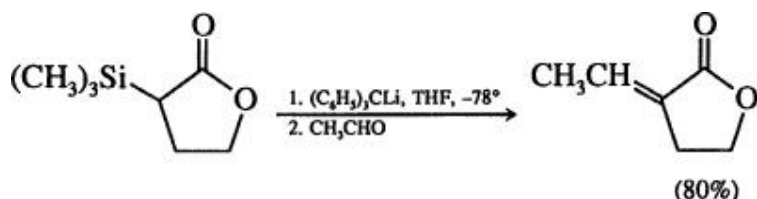
The Peterson reaction is pivotal to one approach to coumarins, where an α -silyl ester is generated in situ from trimethylsilylketene. (211)



Lactones are, of course, a subclass of esters. Lactone enolates undergo C-silylation in the presence of HMPA, (195) (omission of HMPA results in O-silylation (194)), or by use of chlorodiphenylmethylsilane as the silylating agent. (196) Another approach starts from trimethylsilylacetic acid (104). (212)



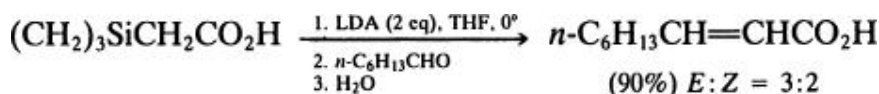
These α -silyl lactones provide α , β -unsaturated lactones in an analogous manner to esters, (195) although use of lithium triphenylmethide as base is advocated to circumvent any problems associated with the formation of Michael byproducts from an amine and an α -ylidenelactone. (212)



The Lewis acid catalyzed condensation of α -silyl lactones with carbonyl compounds has already been illustrated (Eq. 10). (34, 47)

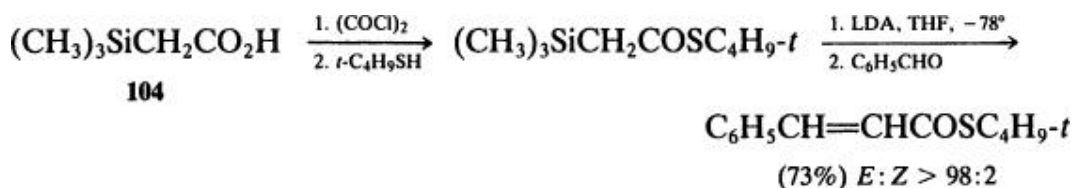
3.2.2.3.2. α -Silyl Acids (189)

The dianion of trimethylsilylacetic acid (104) can be used to prepare α , β -unsaturated carboxylic acids. (212)



3.2.2.3.3. α -Silyl Thioesters

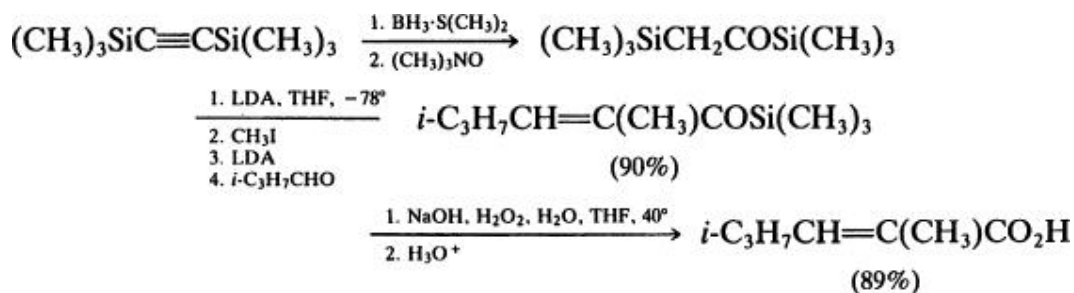
There are many variations on the ester theme. One example is the preparation of α , β -unsaturated thiol esters. The *E* isomer is the major product. (213)



3.2.2.3.4. α -Silyl Acylsilanes

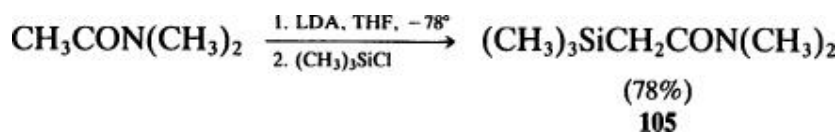
α -Silyl acylsilanes are readily accessible from bis(trimethylsilyl)acetylene. (214) Deprotonation–alkylation–deprotonation–Peterson reaction is available

as a one-pot sequence. (44) The resultant α , β -unsaturated acylsilane is formed as one isomer, and can be converted to the corresponding carboxylic acid by oxidation.

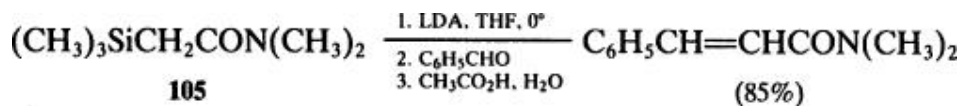


3.2.2.3.5. α -Silyl Amides

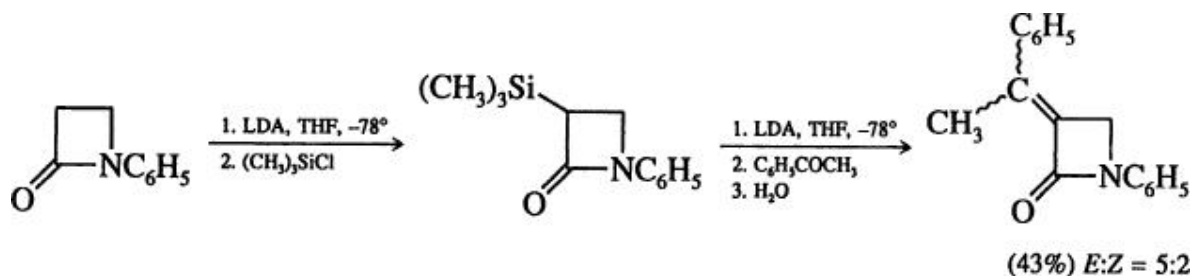
The C-silylated derivative of *N,N*-dimethylacetamide is prepared by deprotonation of the parent amide with lithium diisopropylamide and reaction of the enolate with chlorotrimethylsilane. (195, 215)



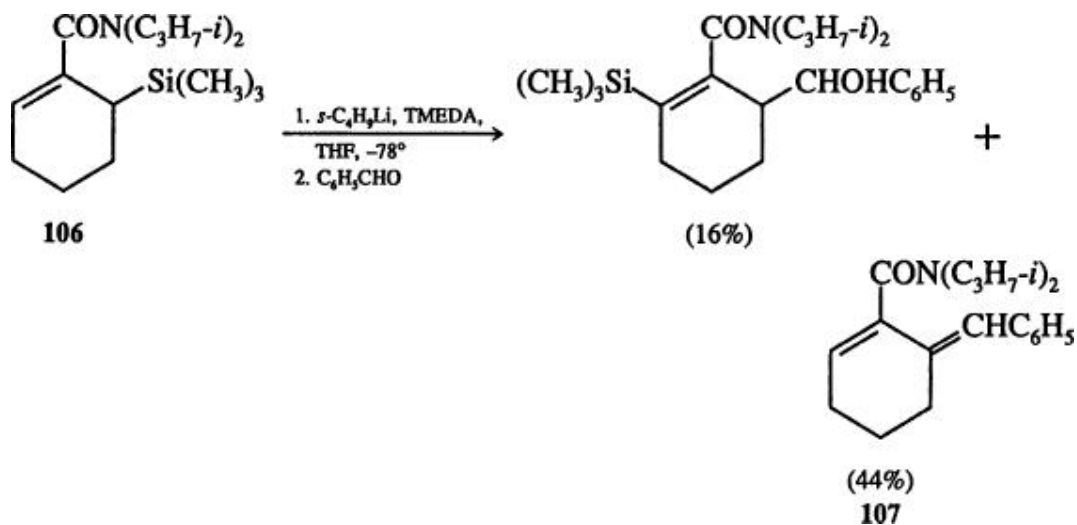
The enolate of amide **105** is more stable than the corresponding ester analog, and reacts in high yields with ketones and nonenolizable aldehydes. (216, 217)



The methodology provides a useful method for the synthesis of 3-alkylideneazetidin-2-ones. (218, 219)

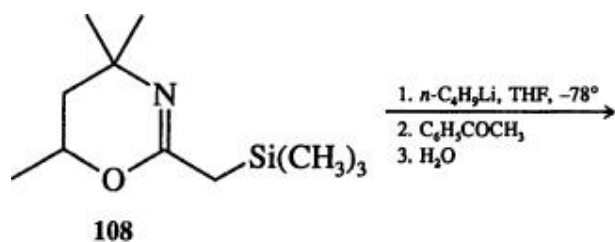


Deprotonation of the unsaturated amide **106** followed by condensation with benzaldehyde results in a mixture of compounds, with the Peterson product **107** as the major component. (220, 221)

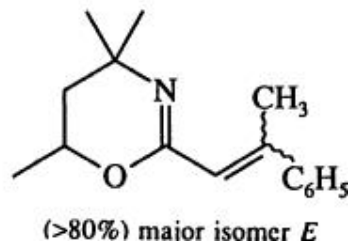


3.2.2.3.6. 2-Silylmethyl-1,3-oxazines

1,3-Oxazines may be considered to be carboxylic acid analogs. Deprotonation of the 2-trimethylsilylmethyl-1,3-oxazine **108** with *n*-butyllithium and subsequent condensation with a methyl ketone provides the alkene as a mixture of isomers. (222)



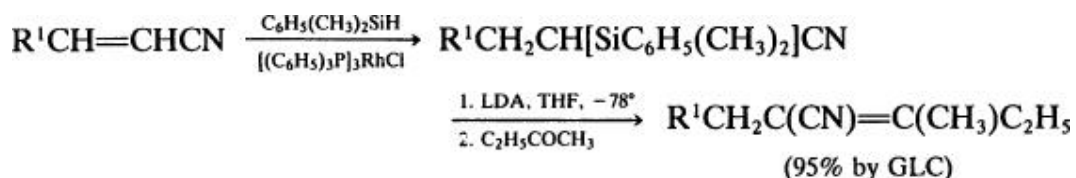
(20)



3.2.3. Preparation of α -Silyl Carbanions Containing Nitrogen

3.2.3.1.1. α -Silyl Nitriles

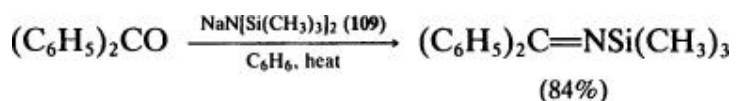
In many ways, nitriles are closely related to carboxylic acid derivatives since hydrolysis of the former provides the latter in high yields. α -Silyl nitriles are available from hydrosilylation of α, β -unsaturated nitriles. (223) Deprotonation with lithium diisopropylamide and reaction with a carbonyl compound provides the homologous unsaturated nitrile. (223, 224)



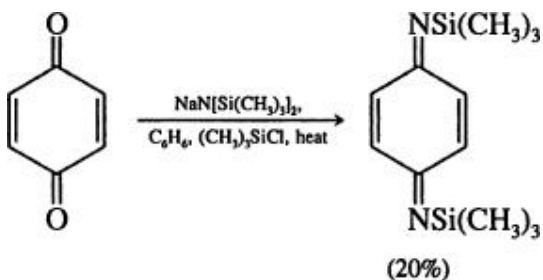
Conjugate addition is observed with the lithio derivative of trimethylsilylacetonitrile and α, β -unsaturated carbonyl compounds. (225)

3.2.3.1.2. Silylamines

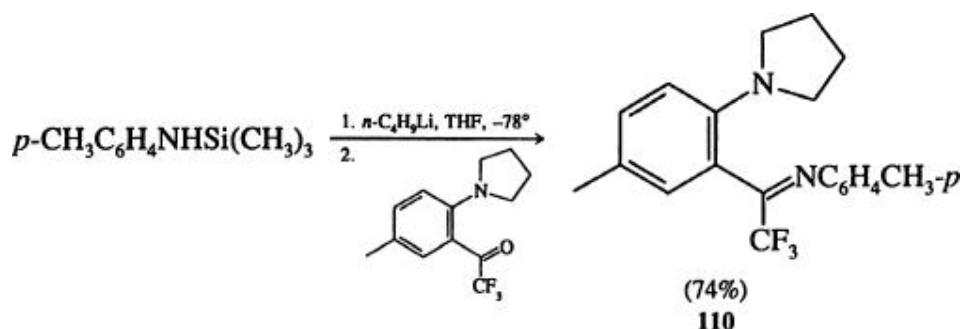
Sodium hexamethyldisilazide (109) is commonly employed as a hindered base. However, it reacts with nonenolizable aldehydes and ketones to provide the imine. (226)



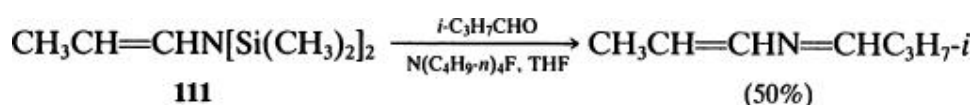
The reagent 109 also reacts with both carbonyl groups of benzoquinone, (226) while in a related reaction, monosilylamines condense with sulfur dioxide (Eq. 29). (227)



This protocol for the preparation of imines has not been fully exploited, but *N*-silylamines do react with carbonyl compounds when heated. (228) An additional example is provided by the preparation of the *N*-arylimine **110**. (229)

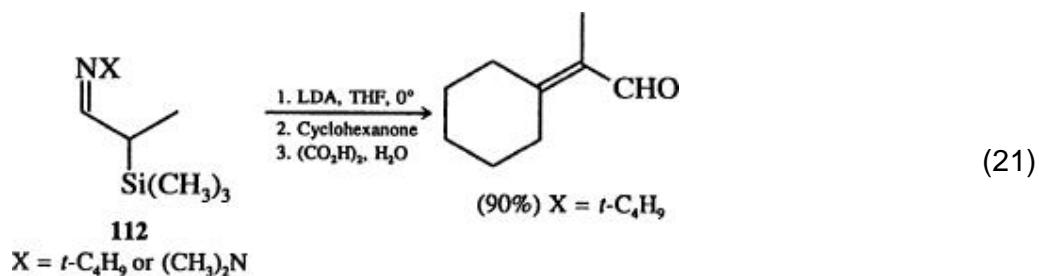


The *N,N*-bis(trimethylsilyl)enamine **111** reacts with carbonyl compounds in the presence of fluoride ion to furnish the imines in moderate yields. (230)

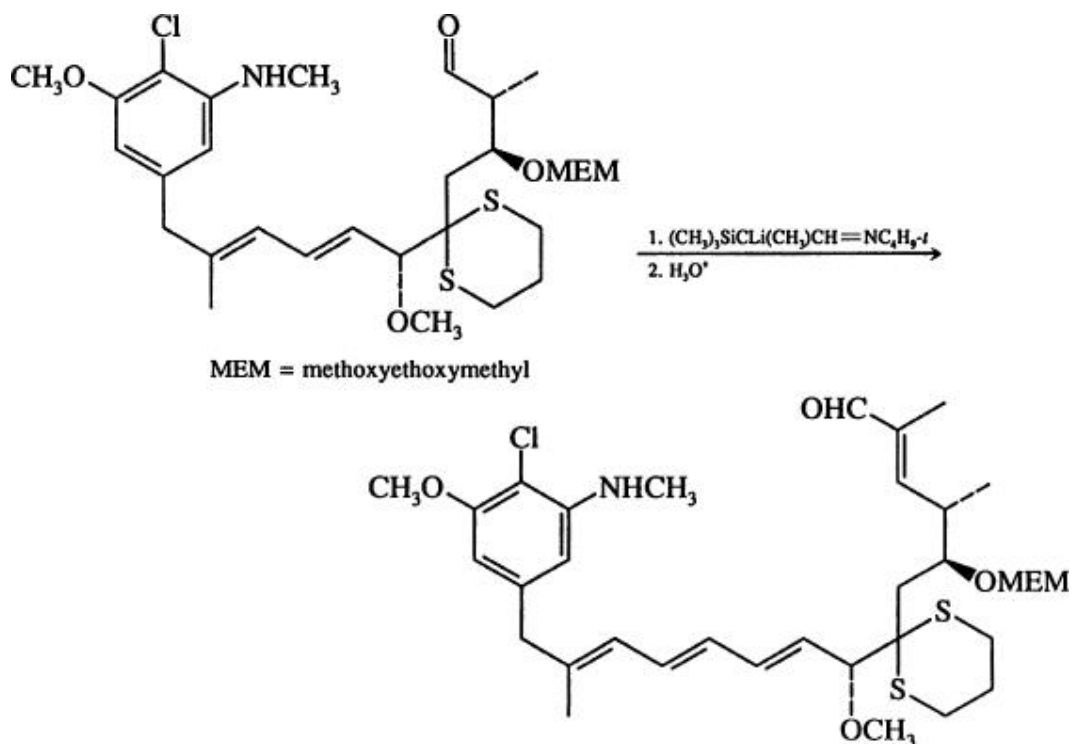


3.2.3.1.3. α -Silyl Imines and Related Derivatives

α -Silyl imines, and other derivatives such as hydrazones, (231) provide useful methodology for the preparation of α , β -unsaturated carbonyl compounds; the nitrogen-containing functional group acts as a protected carbonyl group. (232, 233) This strategy has been employed



in a synthesis of *N*-methylmaysenine. (234) An improvement on reagent



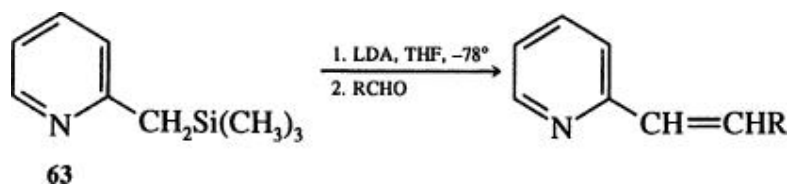
112, which circumvents the problem of competing *N*-silylation during its preparation, is to use the triethylsilyl analog **113**. (235)



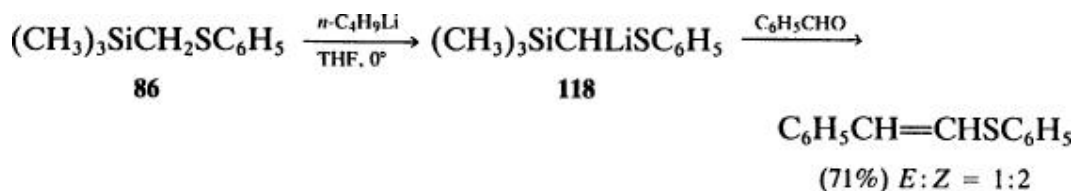
113

α , β -Unsaturated dimethylhydrazones are obtained as shown in Eq. 21 prior to hydrolysis. (236)

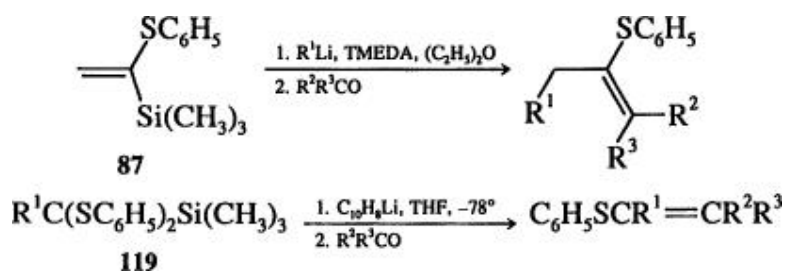
2-Alkylidenepyridine derivatives are readily available from 2-(trimethylsilylmethyl)pyridine (**63**). (96)



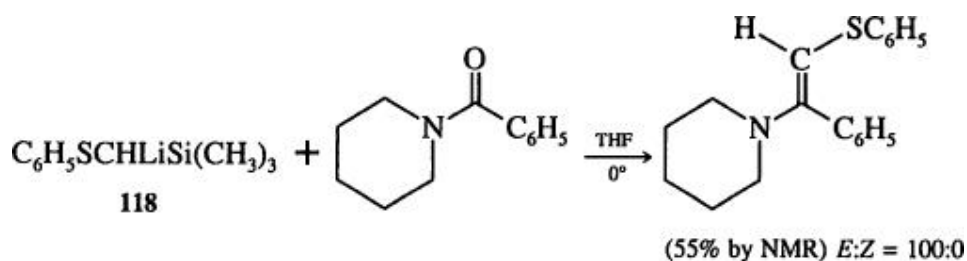
The lithio derivative derived from trimethylsilyldiazomethane reacts with



the addition of an alkyl lithium to 1-phenylthio-1-trimethylsilylethene (**87**), (150, 153, 156, 157, 240) and reductive lithiation of bis(phenylthio)ketals **119**. (153, 157, 241)

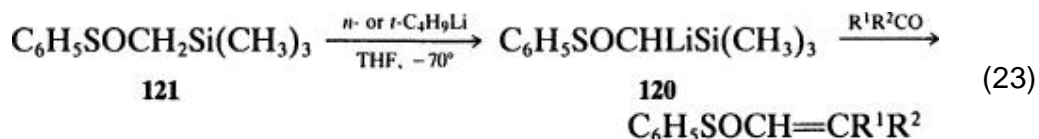


Addition of the organolithium **118** to α , β -unsaturated ketones results in 1,2 addition and the formation of 1-phenylthio-1,3-butadienes. (239, 242) Reaction of the sulfide-containing carbanion **118** with amides provides a route to enamines. (243, 244)

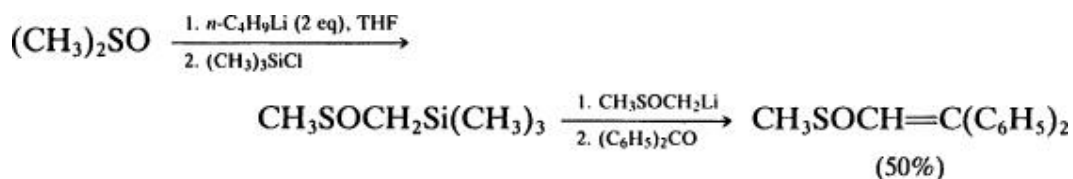


3.2.3.2.2. α -Silyl Sulfoxides

1-Trimethylsilyl-1-phenylsulfinylmethyl lithium (**120**) is available from the parent sulfoxide **121** by reaction with *n*- or *tert*-butyllithium. Condensation of the alkyl lithium **120** with carbonyl compounds provides the vinyl sulfoxides. (245) However, this approach is complicated by the thermal



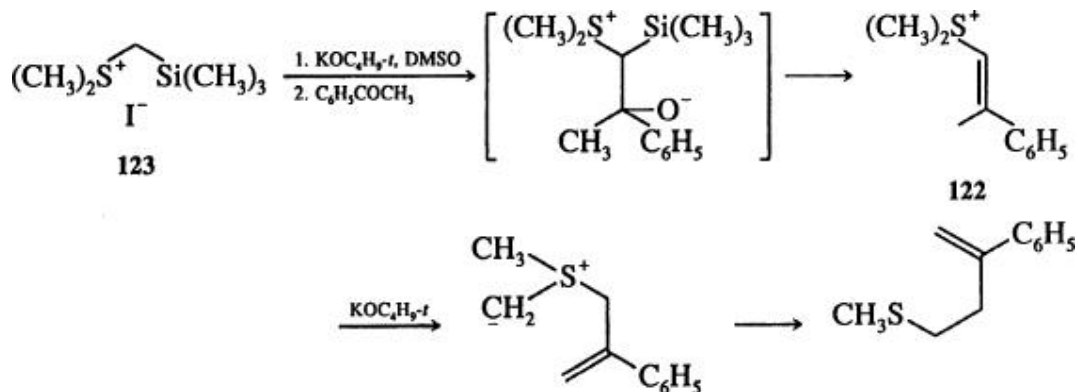
lability of the sulfoxide **121**, which undergoes a sila-Pummerer rearrangement to a significant degree above 0°. This problem can be circumvented to a certain extent by generation of the α -silyl sulfoxide in situ. The sequence of Eq. **23** cannot be used to react the silyl derivative **121** prepared from methyl phenyl sulfoxide since carbon–sulfur bond cleavage occurs. (**245**)



A sulfoxide allows the introduction of an asymmetric center at sulfur. However, when a chiral sulfoxide is used in a sequence analogous to Eq. **23**, stereoselectivity is not observed in the vinyl sulfoxide formation. (**246**) As with the sulfide, the sulfoxide **120** undergoes 1,2 addition to conjugated ketones. (**245**)

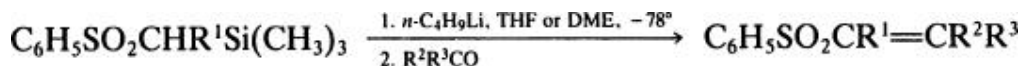
3.2.3.2.3. α -Silyl Sulfuranes

Reaction of trimethylsilylmethylenedimethylsulfurane with carbonyl compounds leads to a vinyl sulfonium product **122**. This sulfonium salt can then undergo further reaction depending upon the nature of the substituents and conditions. (**247**) When the sulfonium salt **123** is deprotonated by *sec*-butyllithium, the vinyl sulfide is isolated. (**248**)

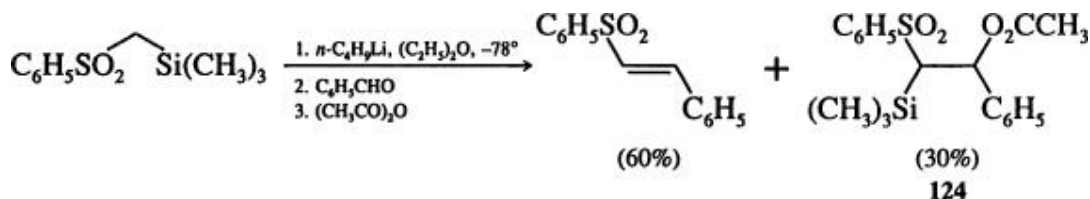


3.2.3.2.4. α -Silyl Sulfones

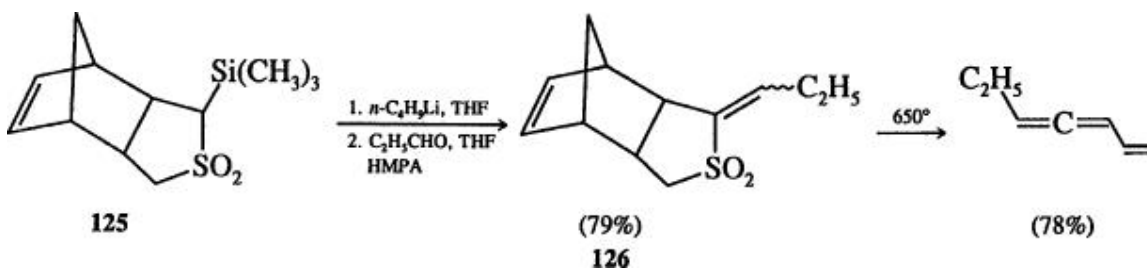
This class of compounds is readily deprotonated because of the excellent anion-stabilizing properties of the sulfone group. (249) Vinyl sulfones are obtained in good to excellent yields. (250-253) The use of 1,2-dimethoxyethane (DME) is advocated as the solvent of choice for this reaction. (251) When an alkyl substituent is attached to the carbon atom bonded to the silicon and sulfur groups, the reaction does proceed but yields can be low, particularly with enolizable ketones. (157)



The intermediate β -hydroxysilane can be trapped by acylation when the condensation is performed in diethyl ether. Nucleophilic elimination from the acetate **124** to the vinyl sulfone is not, however, stereoselective. (253)



The tricyclic sulfone **125** provides the vinyl sulfone **126** by a Peterson protocol. Thermolysis of **126** affords a vinylallene. (254)

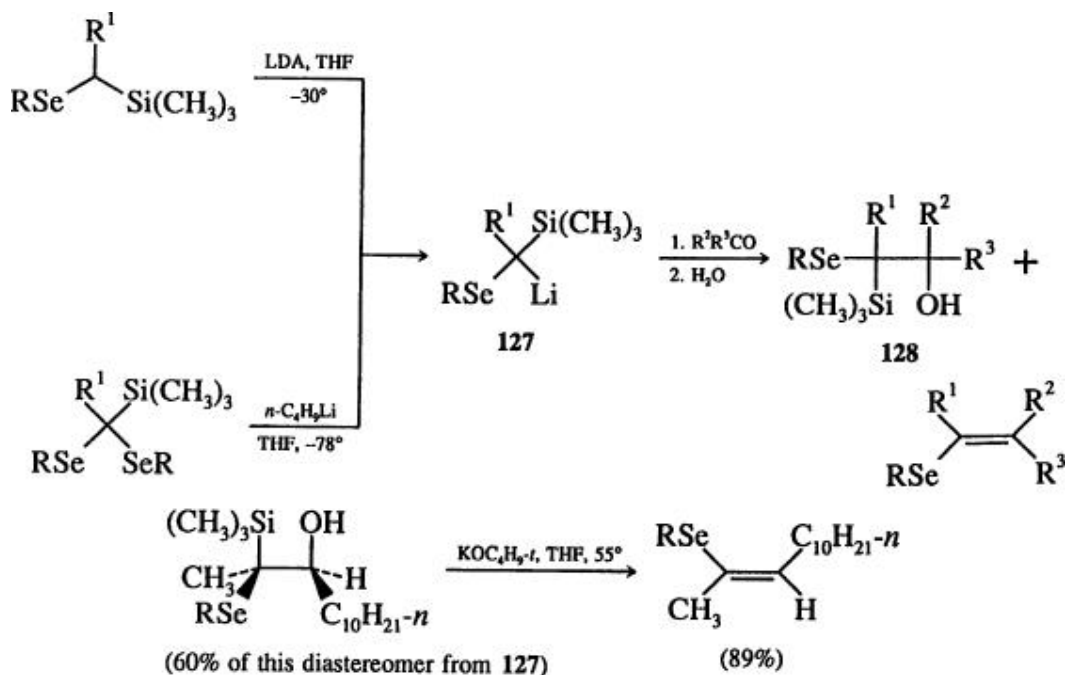


3.2.4. Preparation of α -Silyl Carbanions Containing Selenium

3.2.4.1.1. α -Silyl Selenides

The chemistry of α -silyl selenides has been included in reviews of organoselenium chemistry. (88, 255)

The requisite carbanion **127** is prepared either by direct deprotonation of the parent α -silyl selenide or by transmetalation of a selenide. The latter route usually provides higher yields. (256) For many examples, the β -hydroxysilane can be isolated in good yield and the diastereomers separated. Base treatment then results in just one vinyl selenide isomer. (257)



The selenium moiety can also be eliminated from the alcohol **128** by use of the appropriate reagents, such as phosphorus oxychloride in the presence of triethylamine, to yield the vinylsilane. (257)

Although the anion derived from 1,3-bis(phenylseleno)-3-trimethylsilylpropene (**129**) condenses with carbonyl compounds, reaction occurs at the carbon atom gamma to the silyl moiety and, thus a Peterson reaction pathway is not available. (258)

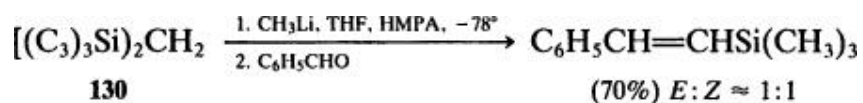


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3.2.4.2. Preparation of α -Silyl Carbanions Containing Silicon (16, 88)

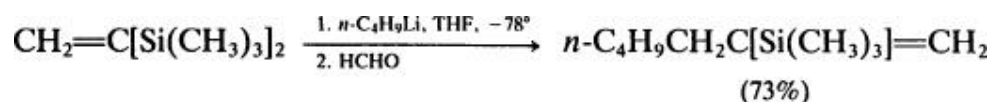
This class of compounds requires two silyl groups on the carbon atom carrying the negative charge. As with a monosilyl carbanion, the silicon atoms do stabilize the negative charge but do not facilitate kinetic deprotonation. The

parent compound, bis(trimethylsilyl)methane (**130**), is deprotonated by methyllithium. ([170](#), [259](#)) Alternative methods must be employed for higher homologs—these

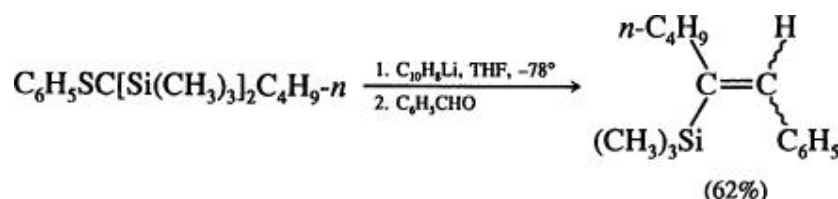


indirect routes parallel those used for the preparation of α -silyl carbanions.

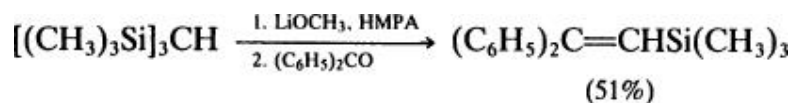
An alkyl lithium adds cleanly to 1,1-bis(trimethylsilyl)ethene, and the resultant anion reacts with carbonyl compounds to afford the vinylsilanes. ([240](#), [259](#))



A phenylthio group can be transmetalated to provide the requisite anion, ([241](#))



while a silicon moiety can be displaced by a similar strategy. ([166](#))

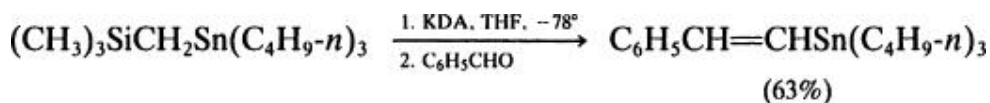


When an allyl anion can be formed, deprotonation of a bis(silyl) compound is relatively straightforward. ([173](#)) The condensation reactions of these allyl anions can be controlled stereoselectively (Eqs. [5](#) and [12](#)). ([28](#), [81](#), [82](#))

3.2.4.3. Preparation of α -Silyl Carbanions Containing Tin

(Tri-*n*-butylstannyl)(trimethylsilyl)methane is deprotonated by potassium diisopropylamide (KDA), albeit in low yield (ca. 50%). Subsequent condensation of the potassium carbanion with a nonenolizable aldehyde or

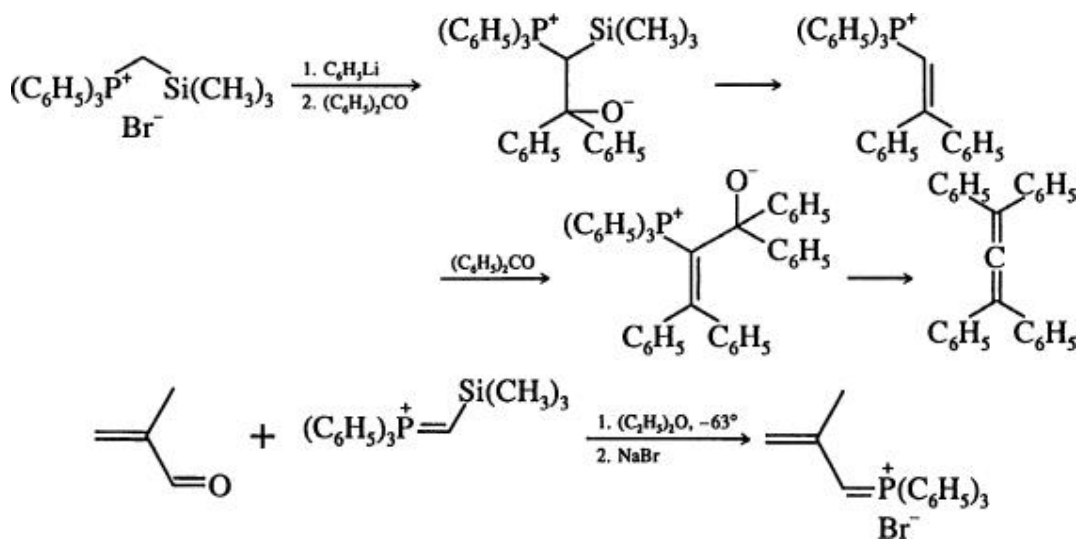
ketone yields the vinylstannane by way of silicon elimination. Extrusion of the stannyl group is not observed as a competing elimination pathway. (260)



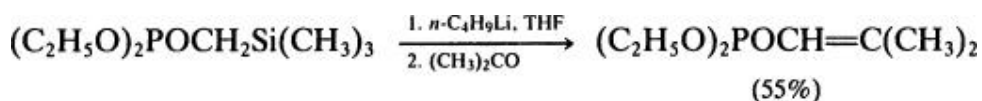
3.2.4.4. Preparation of α -Silyl Carbanions Containing Phosphorus

Reaction of the ylide derived from (trimethylsilylmethyl)triphenylphosphonium bromide (261) with benzophenone leads to tetraphenylallene. (262) This reaction illustrates that the silyl moiety is eliminated more rapidly than the phosphorus group.

The analogous reaction with α , β -unsaturated carbonyl compounds leads to the alkyl-1,3-dienylphosphonium salt. (263)

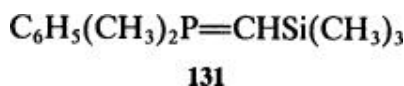


Other vinylphosphorus compounds, such as vinylphosphonates, (239, 264) vinylphosphines, (3) and vinylphosphine sulfides, (3) are also available by the Peterson olefination reaction.

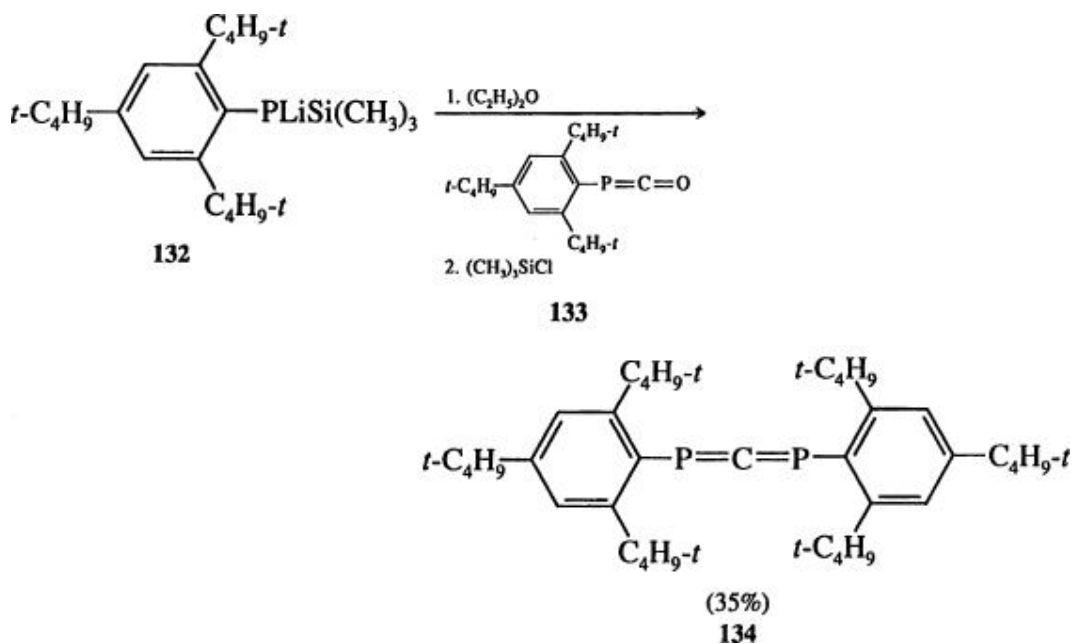


The use of a β -phosphine oxide to stabilize an α -silyl carbanion provides a route to allylphosphine oxides (Eq. 13). (98)

Although most α -silyl carbanions react with a wide variety of electrophiles in a manner analogous to carbonyl compounds, (trimethylsilylmethylene)-dimethylphenylphosphorane (**131**) condenses with isocyanates, isothiocyanates, and carbon disulfide to yield products resulting from insertions into the carbon-silicon bond through irreversible migrations of the silyl group. (265)



The phosphide **132** condenses with the phosphaketene **133** to afford the phosphallene **134**. (266)

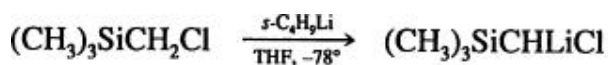


3.2.4.5. Preparation of α -Silyl Carbanions Containing Halogens

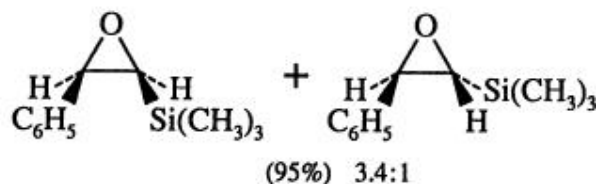
Deprotonation of chloromethyltrimethylsilane or α -chloroethyltrimethylsilane (267) with *sec*-butyllithium provides the α -halo carbanion. Condensation of this anion with an aldehyde or ketone provides the chlorohydrin, which upon treatment with sodium hydride yields the α, β -epoxysilane. (268, 269) Thus,

the chlorine is eliminated in preference to attack of the alkoxide at silicon.

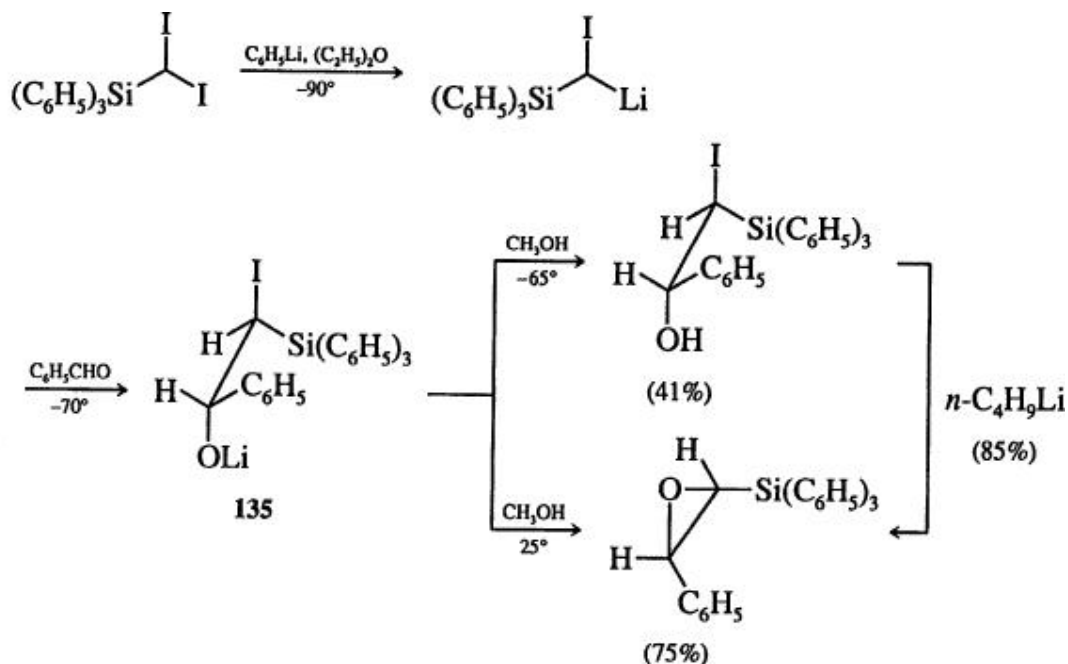
The approach has been used in a short synthesis of (*R*)-(+)-frontalin. (270)



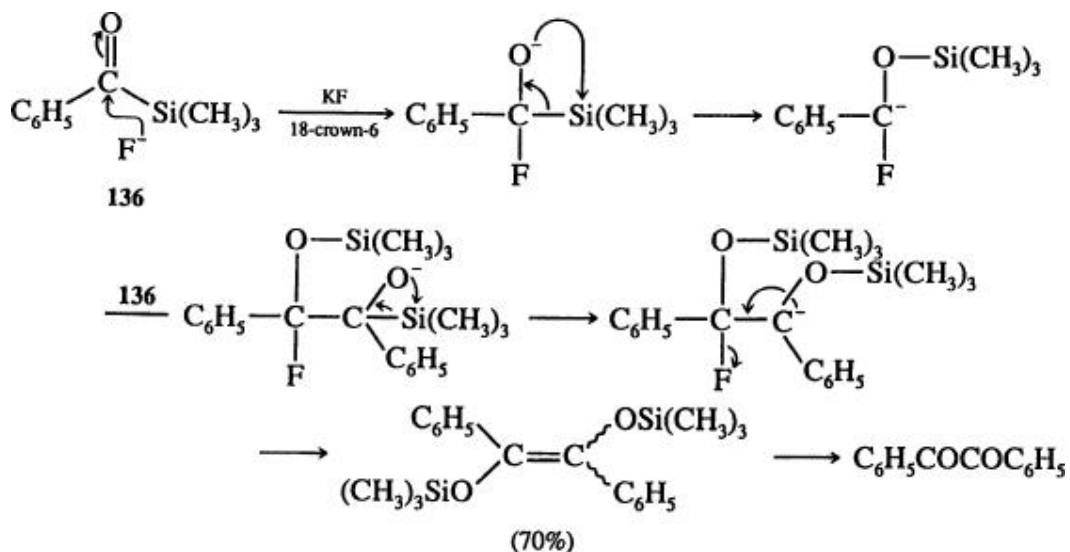
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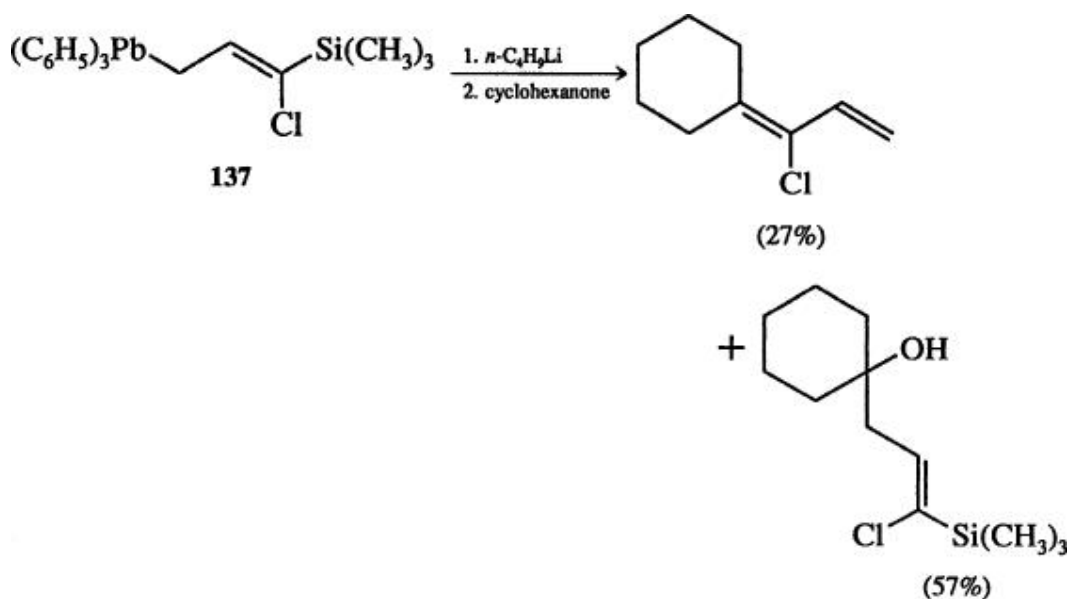
In an analogous manner, condensation of the carbanion derived from triphenylsilylmethylene iodide provides the epoxide through preferential displacement of the iodide; (271) the *threo*-diastereomer of the β -alkoxysilane **135** is formed as the major isomer. (272)



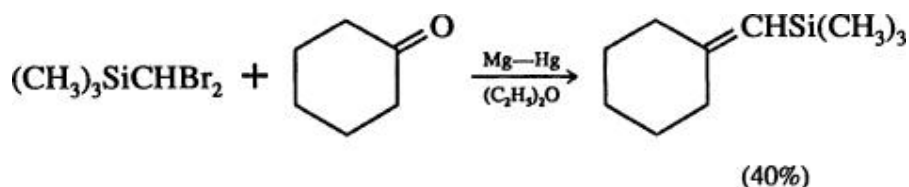
A closely related reaction is observed when the acyl silane **136** is treated with fluoride ion to yield benzil. Fluoride is eliminated preferentially to the trimethylsilyloxy group. This reaction also involves the migration of a silyl group from carbon to oxygen. (273)



Reaction of the allyl anion, prepared by a transmetalation from the lead compound **137**, with carbonyl compounds leads to a mixture of products, including those arising from a Peterson olefination pathway. (274)

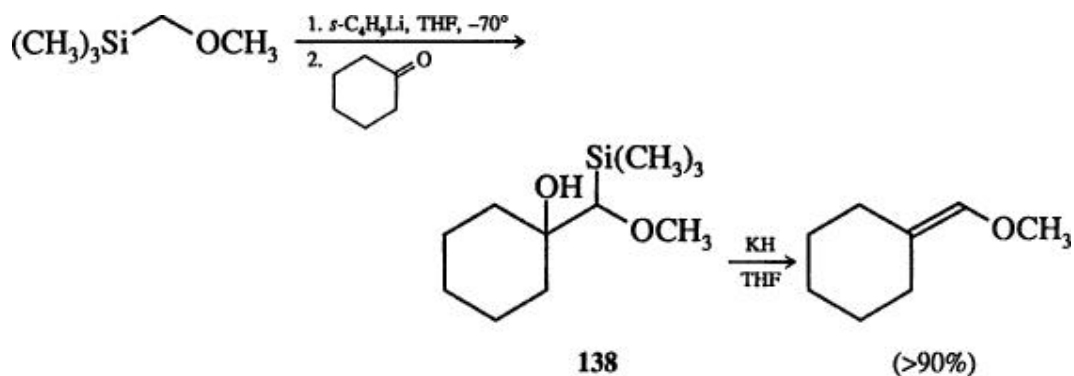


Treatment of dibromo(trimethylsilyl)methane and cyclohexanone with magnesium amalgam results in formation of the vinylsilane. However, the procedure is not general, and the exact mechanism is open to question. (275)

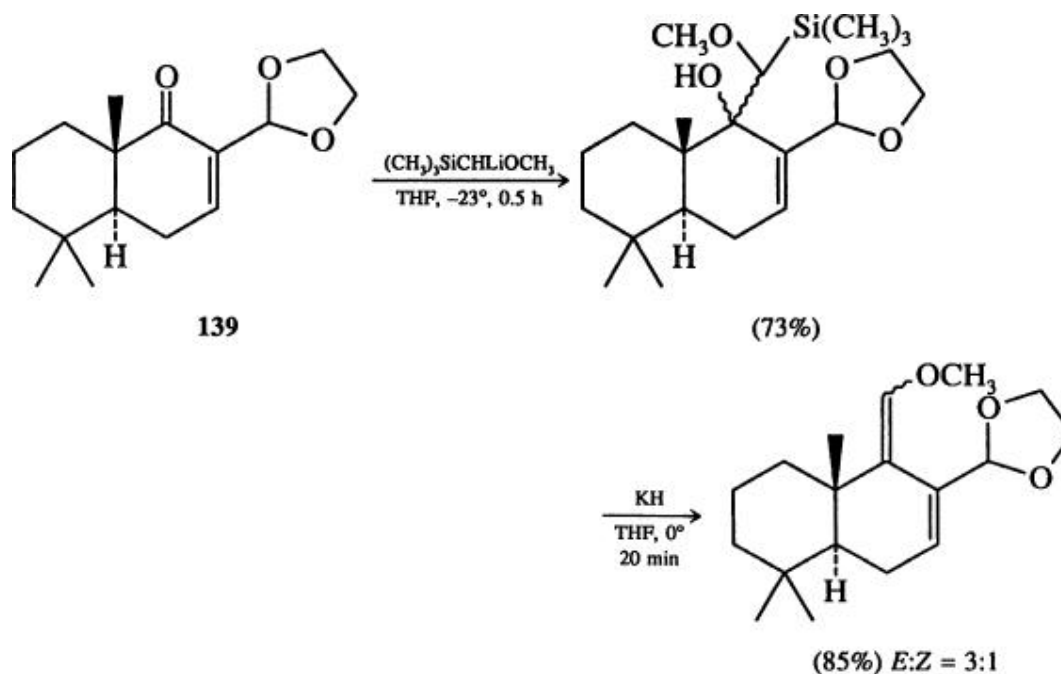


3.2.4.6. Preparation of α -Silyl Carbanions Containing Oxygen

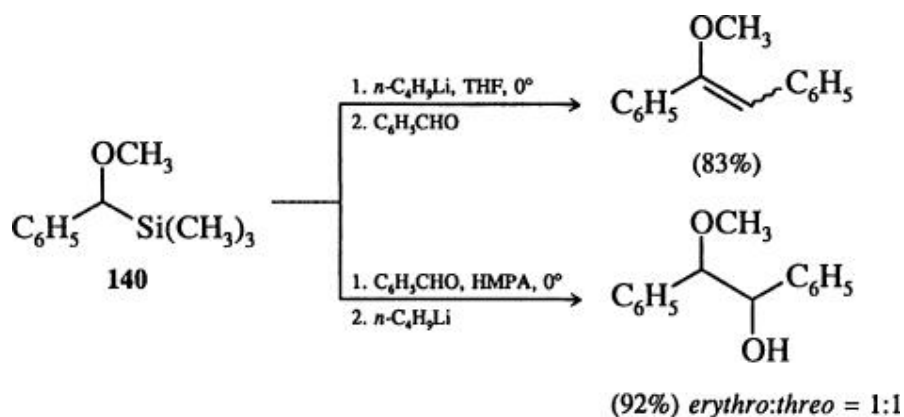
Methoxymethyltrimethylsilane is deprotonated by *sec*-butyllithium to give, upon condensation with a carbonyl compound, the β -hydroxysilane **138**; elimination is effected by potassium hydride. (276, 277) This methodology has been employed in a synthesis



of warburganal, when other nucleophiles, including Wittig reagents, failed to react with the enone **139**. (278)



In contrast, benzylsilanes **140** undergo an anion–radical induced desilylation in polar solvents to yield the β -alkoxyalcohol; (**279**) the Peterson reaction is still observed in less polar solvents.



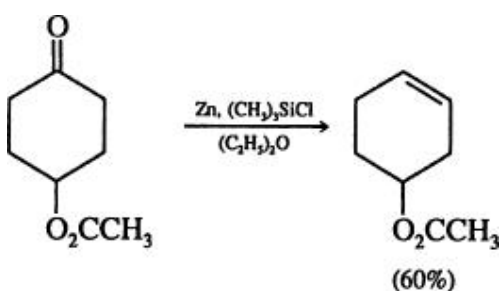
3.2.4.7. Preparation of α -Silyl Carbanions Containing Boron

Treatment of pinacol trimethylsilylmethaneboronate (**141**) with lithium 2,2,6,6-tetramethylpiperidine (LTMP) followed by a carbonyl compound gives the alkeneboronic ester. (**280**) The reaction cannot be applied to higher homologs of **141** because the lithiation procedure fails. (**281**)

3.2.4.8. Other Transformations Closely Related to the Peterson Olefination Reaction

Reactions closely related to the Peterson olefination, including the use of electrophiles containing carbonyl groups, are discussed elsewhere in this chapter.

Other transformations that could involve a Peterson-type mechanism are the deoxygenation of ketones by zinc and chlorotrimethylsilane, (284) and the deoxygenation of epoxides by magnesium and the same chlorosilane. (285) The exact mechanisms of these reactions have not been rigorously established.



3.2.4.9. Preparation of α -Silyl Carbanions Containing Two or More Functional Groups

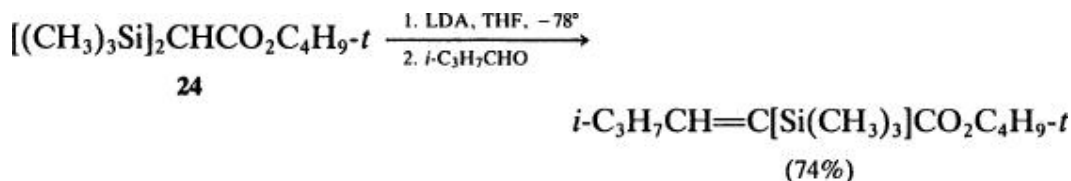
In many respects, these classes of compounds just combine two or more of the functional groups described above onto the same carbon atom together with a silyl group. Most of the reactions of these compounds mirror those of the monosubstituted series, although in some cases the sheer size of the carbanion promotes reaction of this species as a base rather than a nucleophile.

The examples cited in this section are subdivided by the nature of the substituents and listed in the same order as used for the monosubstituted α -silyl carbanions. When one of the functional groups is carbon-carbon unsaturation so that an allyl (or propargyl) anion results from the deprotonation procedure, the chemistry of this system is discussed in the appropriate monosubstituted section provided that condensation with a carbonyl compound results directly in a Peterson-type elimination.

3.2.4.9.1. α -Silyl Carbanions Containing an Ester and Silyl Groups

The enolate anion derived from *tert*-butyl bis(trimethylsilyl)acetate (24) reacts with aldehydes to give the α -silyl- α , β -unsaturated esters in good yields.

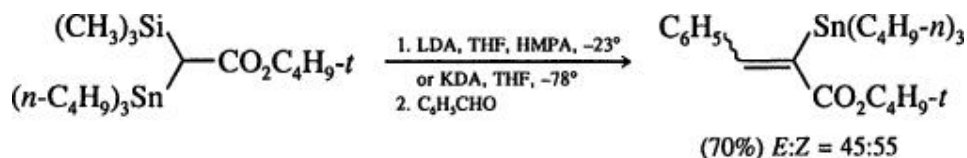
Condensation occurs in a 1,2 manner with conjugated enals but fails with enones. (286)



The use of various cations as the enolate counterion can be used to control the stereochemical outcome of the reaction (Eq. 9). (46)

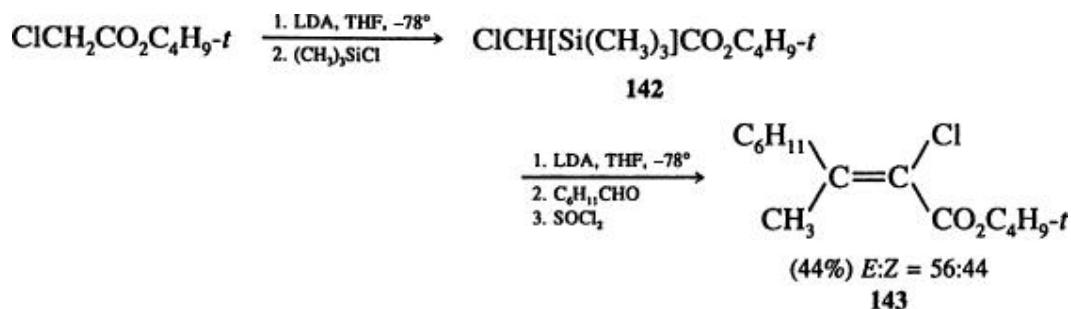
3.2.4.9.2. α -Silyl Carbanions Containing an Ester and Tin Groups

Reaction of the lithium or potassium enolate derived from *tert*-butyl (trimethylsilyl)tri-*n*-butylstannylacetate with carbonyl compounds provides a useful method for the preparation of α -stannyl- α , β -unsaturated esters. (260, 287)



3.2.4.9.3. α -Silyl Carbanions Containing an Ester and Halogen Groups

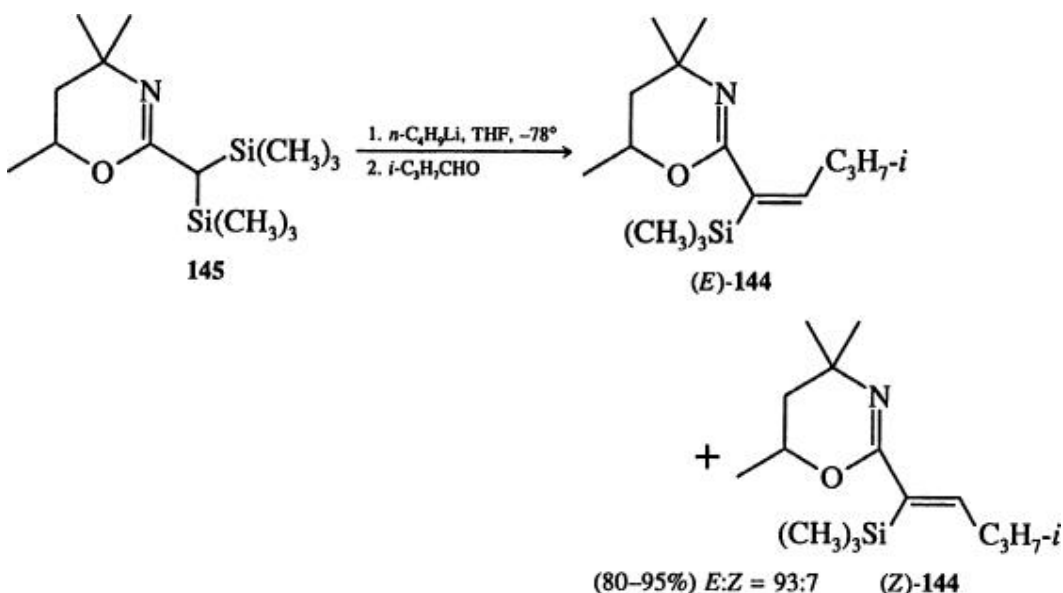
tert-Butyl chloroacetate is deprotonated by lithium diisopropylamide, and subsequent silylation results in formation of the adduct 142.



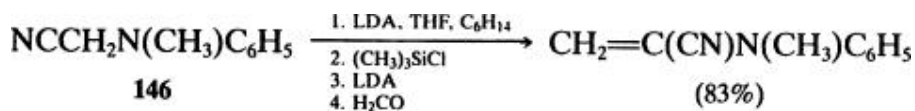
The ester 142 is deprotonated and condensed with a carbonyl compound by the standard procedures. Workup is optimized by use of thionyl chloride, which suppresses isolation of the β -hydroxysilane rather than the α -halo ester 143.

(288) *tert*-Butyl bromo(trimethylsilyl)acetate provides α -bromo- α , β -unsaturated esters in an analogous manner. (289)

3.2.4.9.4. α -Silyl Carbanions Containing a 1,3-Oxazine and Silyl Groups
 In a manner completely analogous to Eq. 20, the vinylsilanes **144** are prepared from the bis(silyl) compound **145**. In all cases the *E* isomer is the major product. (222)

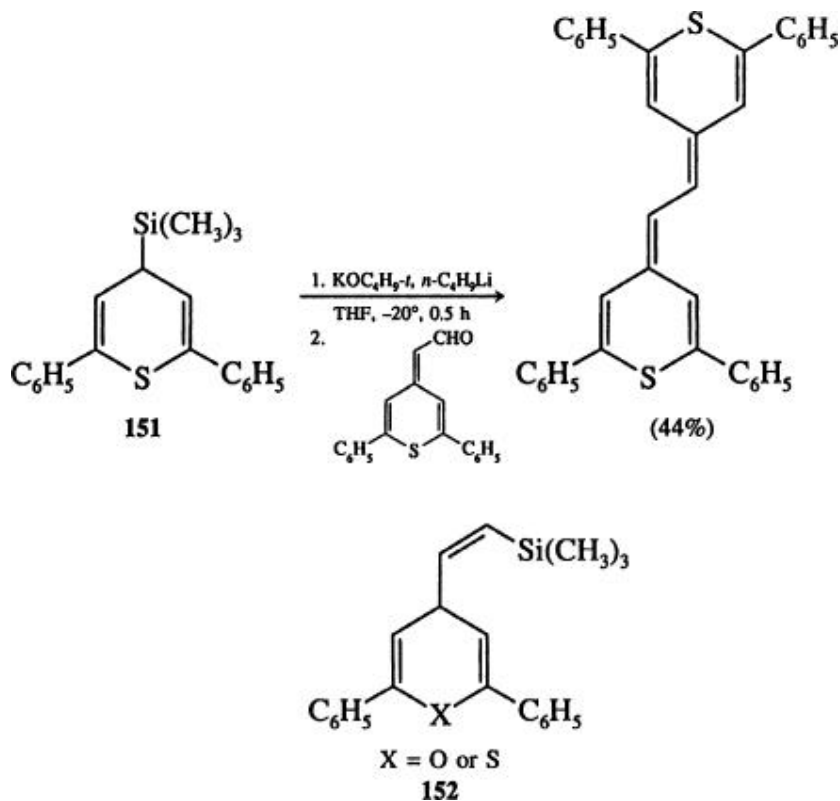


3.2.4.9.5. α -Silyl Carbanions Containing Two Nitrogen Groups
 The α -amino nitrile **146** can be silylated and subsequently condensed with a carbonyl compound in a one-pot reaction. (290, 291)



3.2.4.9.6. α -Silyl Carbanions Containing Nitrogen and Sulfur Groups
 1-(Arylthio)alkenyl isocyanides are available from arylthiomethyl isocyanides **147**. The silylation and condensation steps can be performed in a single flask. (292)

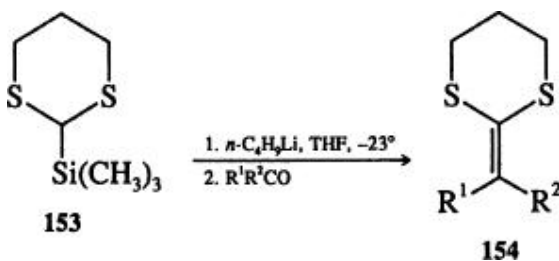
In a similar manner, 1-isocyano-1-toluenesulfonylalkenes are obtained from the sulfone **148**. (293)



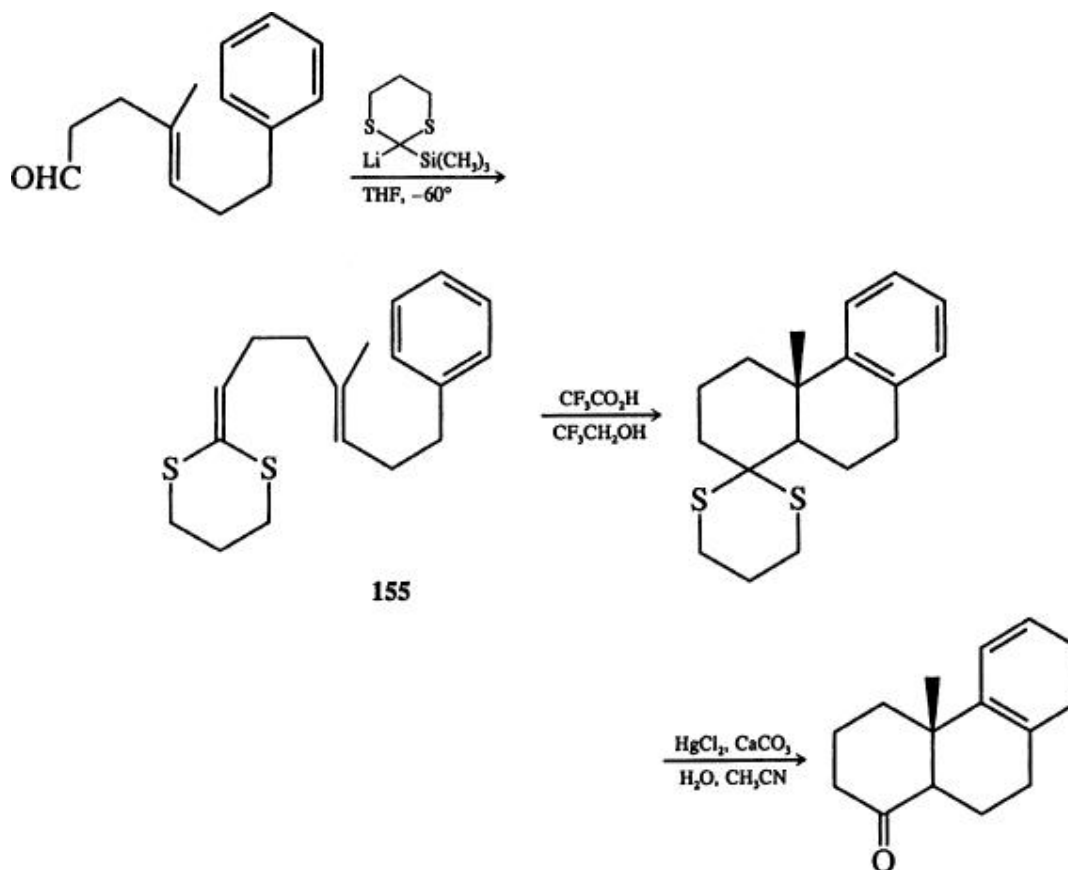
3.2.4.9.9. α -Silyl Carbanions Containing Two Sulfur Groups

This is the largest class of compounds in this category since the product ketene thioacetals can be used as the starting materials for a wide range of synthetic transformations. (299, 300)

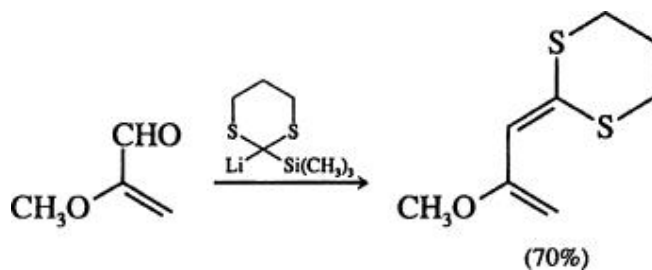
The two sulfur atoms are often part of a 1,3-dithiane system because the required 2-silyl derivative **153** is readily available. (301, 302) Deprotonation of the silane **153** with *n*-butyllithium followed by reaction with a carbonyl compound provides the ketene thioacetals **154** in good yields. (303-309) 1,2 Addition is observed between the organolithium derived from the 1,3-dithiane **153** and



α , β -unsaturated ketones. (305) The general application of this methodology can be illustrated by the preparation of the ketene thioacetal **155** and its use in a cyclization procedure. (310)

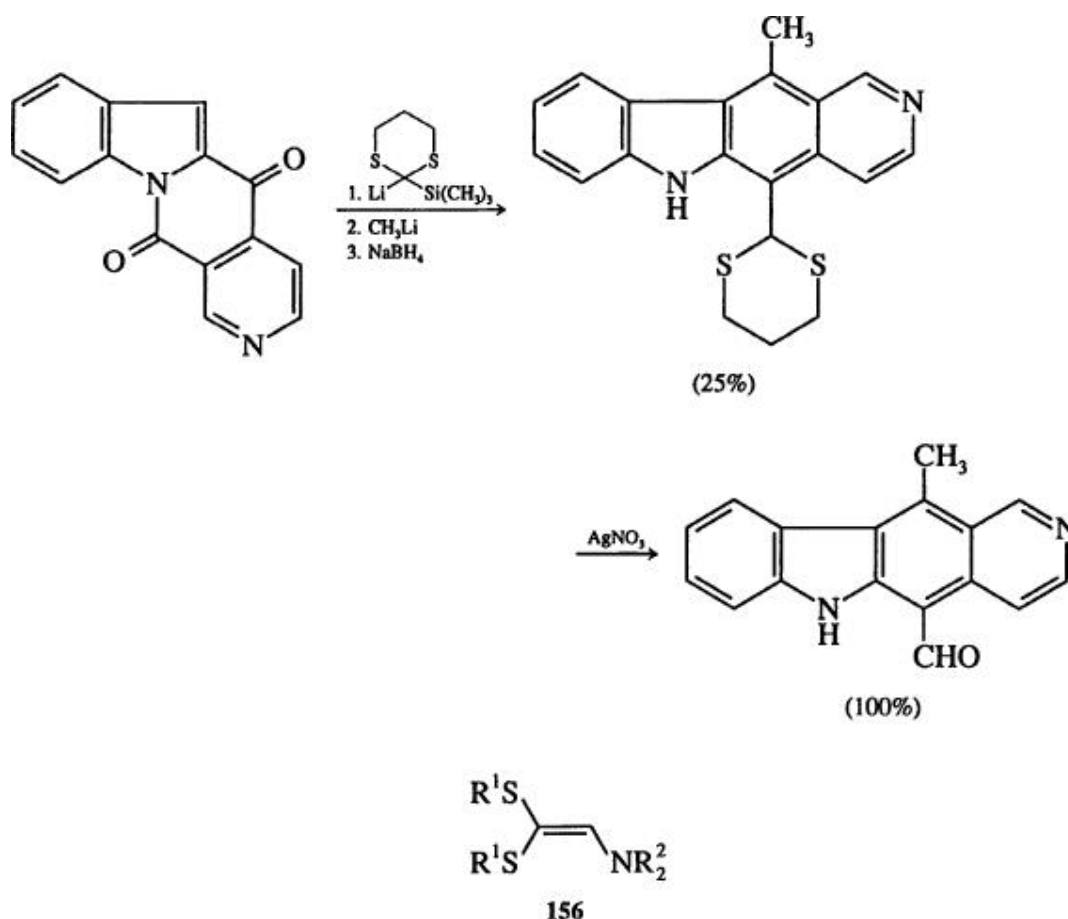


The preference for 1,2 addition can be put to good use for the preparation of substituted 1,3-butadienes. (311) A further example of the methodology is available as part of a synthesis of 17-oxoelliptane. (312)

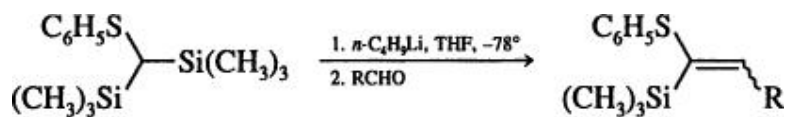


Other sulfur groups, such as phenylthio, can be used to give the homologous ketene thioacetals, (240, 308, 313, 314) and in certain cases, the carbanion is available by a displacement reaction rather than deprotonation. (241) When the sulfur atoms are not part of a cyclic system, 1,4 addition is usually observed with conjugated ketones; the regioselectivity is, however, dependent upon the exact nature of the carbanion, enone, and reaction conditions. (242, 315, 316)

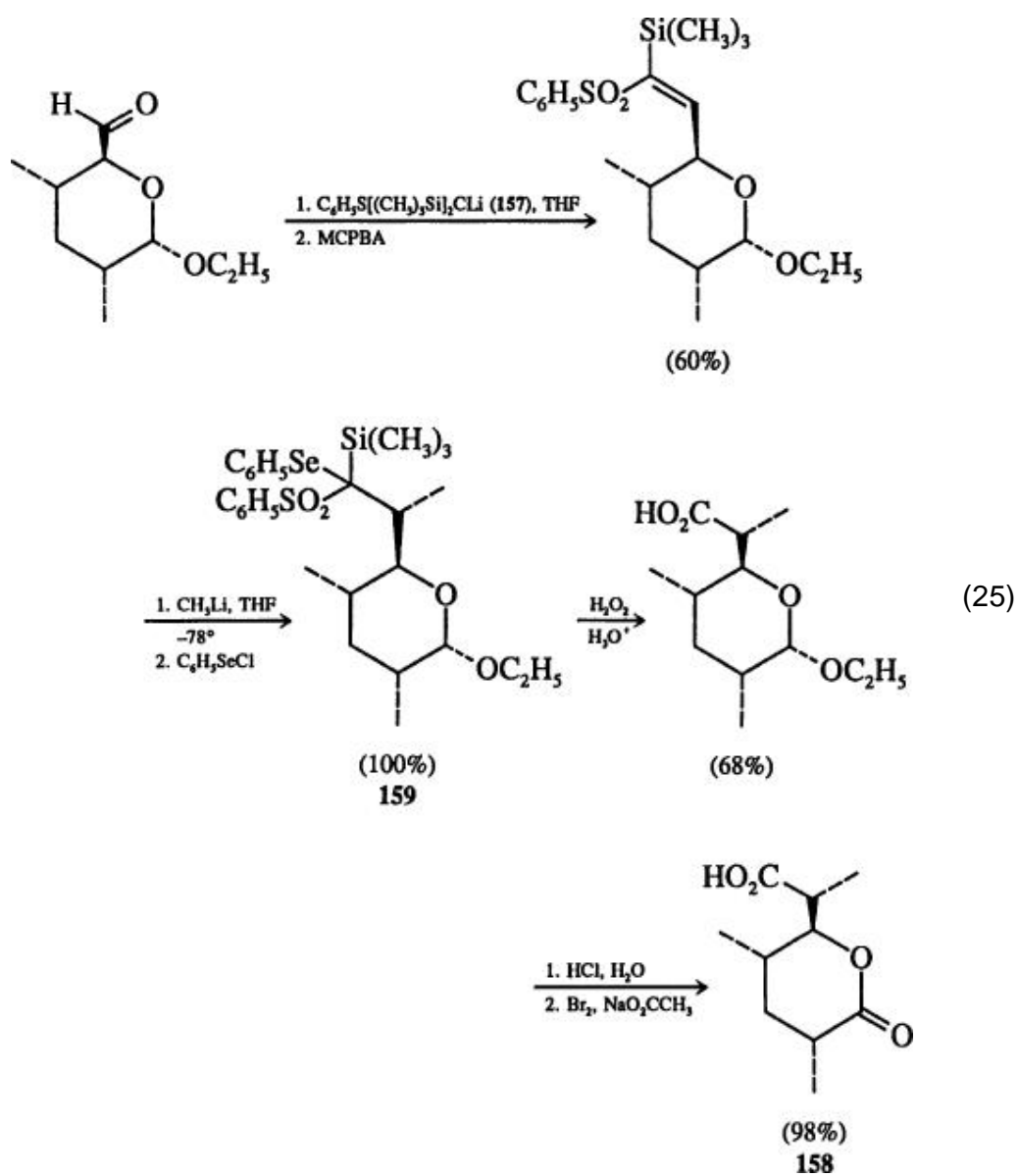
Formamides derived from secondary amines react with bisthio(trimethylsilyl)methylolithiums to furnish the enamines 156. (308)



3.2.4.9.10. α -Silyl Carbanions Containing Sulfur and Silicon Groups
 1-Thio-1-silylalkenes are readily available by the Peterson protocol. (313) The requisite anion 157 is also available by a sulfur displacement reaction. (241)

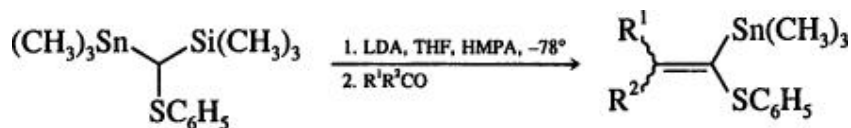


Bis(trimethylsilyl)phenylthiomethylithium (**157**) can be used as a carboxylate anion equivalent by the strategy illustrated in Eq. 25, which outlines a synthesis of the Prelog–Djerassi lactone (**158**). Conversion of selenide **159** to the acid is achieved by a selenium analog of the sila-Pummerer rearrangement. (317, 318)



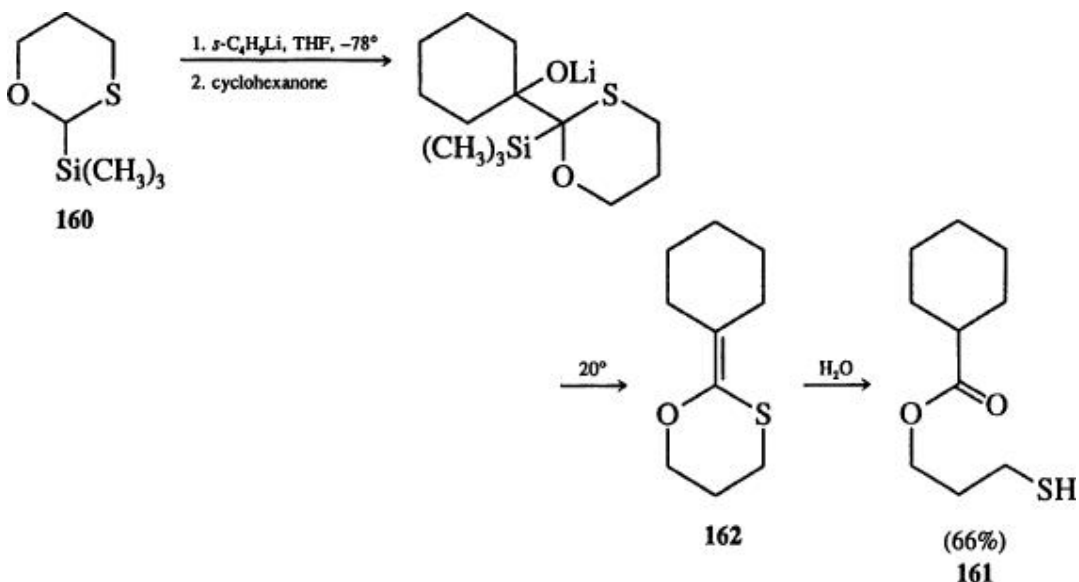
3.2.4.9.11. α -Silyl Carbanions Containing Sulfur and Tin Groups

Vinylstannanes are formed in the expected manner with the silyl group being eliminated exclusively. (260, 313)

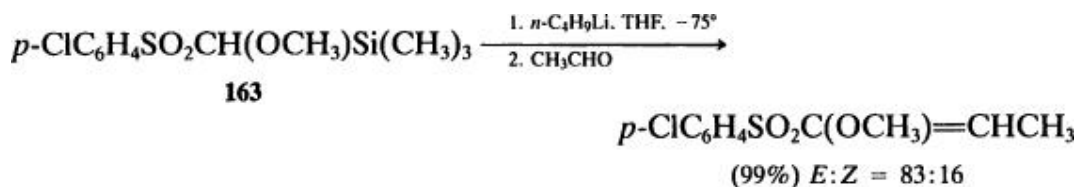


3.2.4.9.12. α -Silyl Carbanions Containing Sulfur and Oxygen Groups

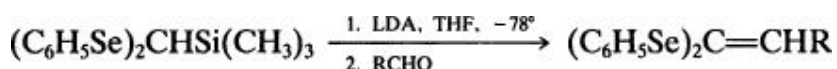
2-Trimethylsilyl-1,3-oxathiane (**160**) (319) is deprotonated by *sec*-butyllithium. When the resultant anion is reacted with benzaldehyde, the β -hydroxysilane results. When benzophenone or cyclohexanone is employed as the carbonyl compound and the reaction mixture is allowed to warm to ambient temperature, thiol esters **161** are formed presumably by way of the ketene acetal **162**. (320)



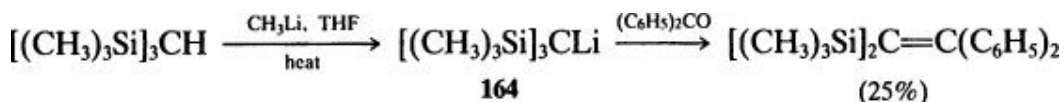
Methoxyphenylthiomethane provides the analogous acyclic ketene acetals in good yields. (321) As with the cyclic thioacetal **160**, 1,2 addition is the major reaction pathway with conjugated carbonyl compounds. The sulfone **163** provides the substituted vinyl sulfones as expected. (322)



3.2.4.9.13. α -Silyl Carbanions Containing Two Selenium Groups
 Ketene selenoacetals are available from a bis(selenosilyl) carbanion. (255, 313)

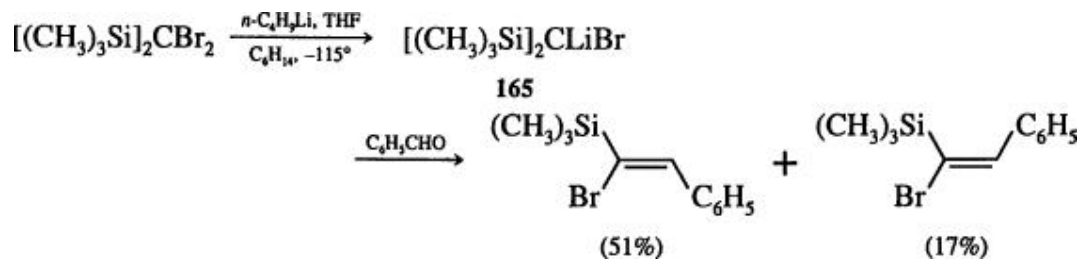


3.2.4.9.14. α -Silyl Carbanions Containing Two Silicon Groups
 Again, one of the major problems is the preparation of the required carbanion, although direct deprotonation of tris(trimethylsilyl)methane is possible using methyllithium as base. (313, 323-325) Condensation with carbonyl compounds is, however, limited to nonenolizable aldehydes and ketones.

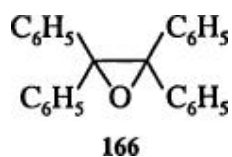


Alternative procedures for the preparation of the carbanion **164** employ addition of an alkyl lithium to 1,1-bis(trimethylsilyl)ethene, (240) reductive lithiation of a phenylthio group by lithium naphthalenide (241) or tri-*n*-butylstannyl lithium, (164) and cleavage of a silyl group by an alkoxide in a polar solvent. (166)

3.2.4.9.15. α -Silyl Carbanions Containing Silicon and Halogen Groups
 Bis(trimethylsilyl)bromomethyl lithium (**165**) reacts with aldehydes to give a mixture of the *E* and *Z* isomers of the 1-bromo-1-trimethylsilylalkene. Reaction of the anion **165** with enolizable ketones leads to proton abstraction from



the carbonyl compound. Treatment of the carbanion **165** with benzophenone leads to the epoxide **166** through elimination of the halogen rather than a silyl moiety. This outcome may be attributed to the most stable conformer



of the intermediate β -hydroxysilane having the oxygen and bromine atoms *anti* to minimize steric interactions between the large phenyl and silyl groups. (326)

3.3. Preparation of Carbonyl Compounds

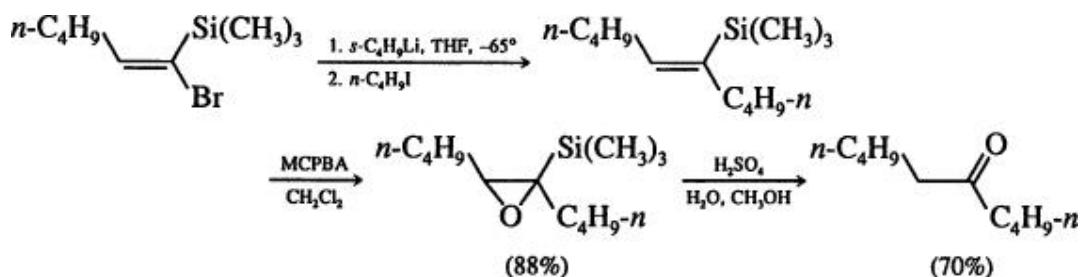
Although the conversion of vinylsilanes and α , β -epoxysilanes into carbonyl compounds is not strictly a Peterson olefination reaction, many of the observations result from the chemistry that has been discussed elsewhere in this chapter.

Overall, the transformation of an α , β -epoxysilane involves opening to the diol which then eliminates to give an enol. This enol then tautomerizes to the carbonyl compound. The stereochemical consequences of the elimination step are of little importance since the double bond is lost in the tautomerization step.

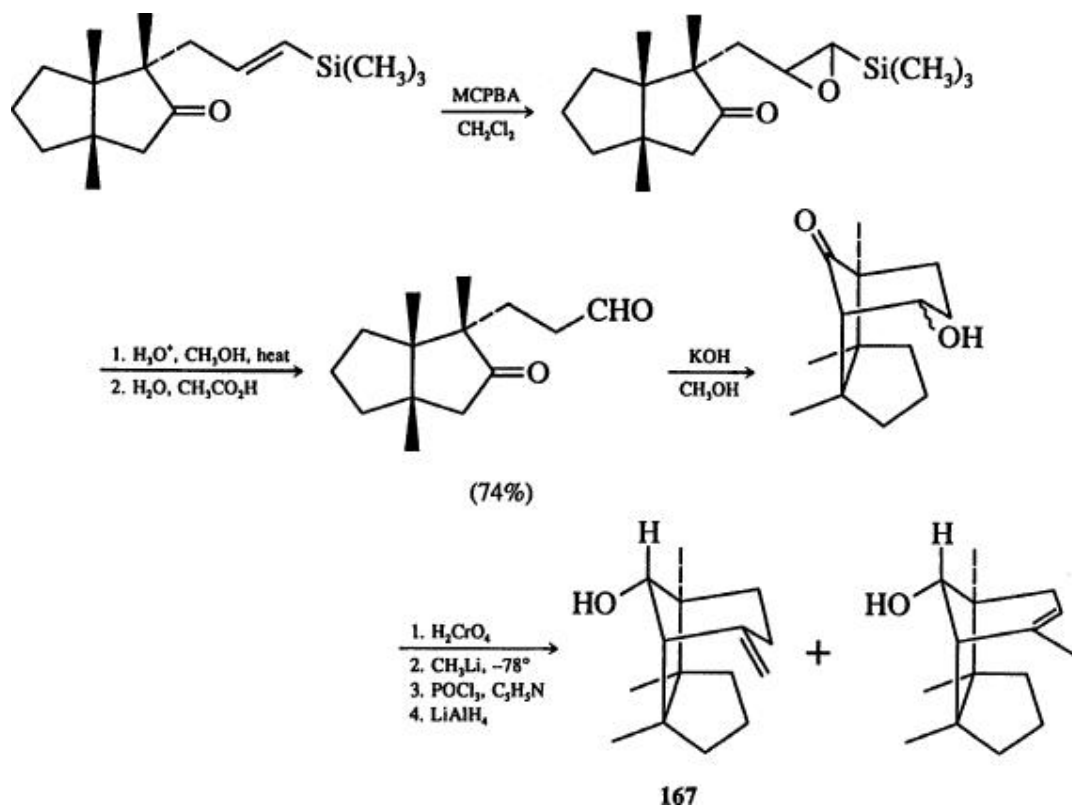
3.3.1.1. Vinylsilanes

All reviews on organosilicon chemistry invariably include a discussion of the methods available for the preparation of this class of compounds. There have also been reviews which have concentrated on the synthesis and reactions of vinylsilanes. (16, 327)

The principal method for conversion of vinylsilanes to ketones is oxidation of the carbon-carbon double bond to an α , β -epoxysilane, which is then hydrolyzed under acidic conditions (Eq. 26). (328) This approach has been used in a variety of applications including an annelation procedure (329) and an acyl anion equivalent. (132, 330)



An example of the use of this protocol is provided by part of the sequence used for the synthesis of the sesquiterpene gymnomitrol (167). (331)



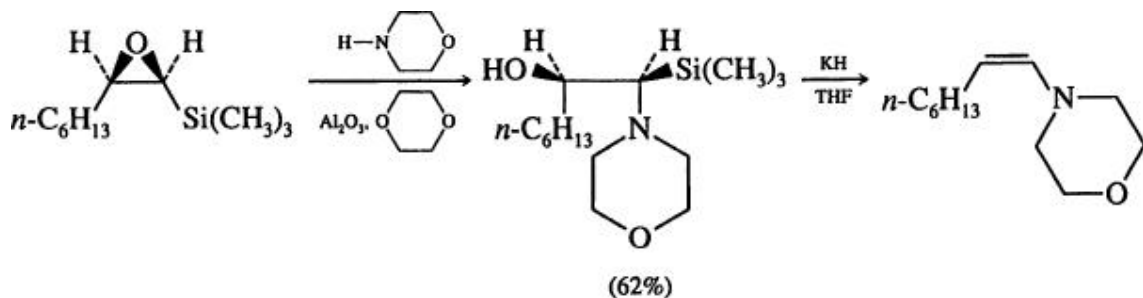
The use of vinylsilanes as carbonyl precursors may increase as the oxidative cleavage of the carbon–silicon bond is exploited. (39)

3.3.1.2. α , β -Epoxy-silanes

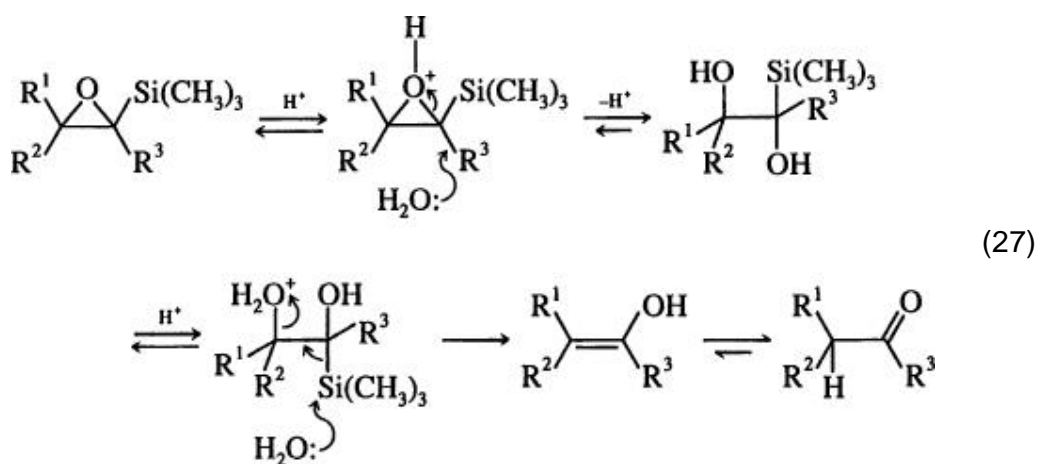
In addition to the oxidation of vinylsilanes, these compounds are available by a number of other routes, (7) including one based on an α -silyl carbanion (Eq. 24). (268)

α , β -Epoxy-silanes are isomerized to the trimethylsilyl enol ethers by treatment with a Lewis acid (332) such as magnesium bromide (66) or by heat. (65, 69, 333) Rearrangements of the substituents can also occur during these isomerizations, and a mixture of products results. (334, 335)

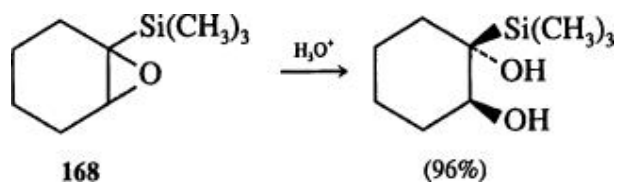
Many reactions of α , β -epoxy-silanes have already been discussed. In addition, these epoxides react with amines to afford enamines which are masked carbonyl compounds. (336)



α , β -Epoxy silanes react with other nucleophiles at the alpha position. (328)
 The stereochemical requirements for the elimination of the silyl group from the resultant β -hydroxysilane are still rigorous.
 1,2-Epoxy-1-trimethylsilylcyclohexane (168) gives addition products with a wide variety of nucleophiles,

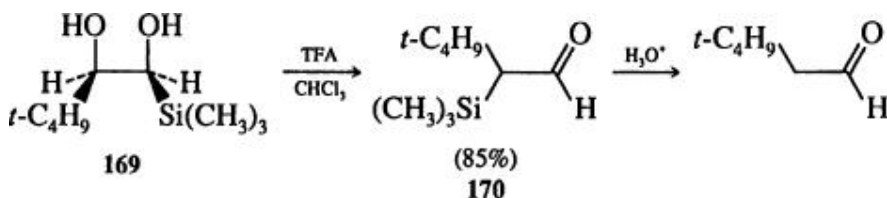


but as the product β -hydroxysilane is *cis*, the *anti* configuration necessary for elimination cannot be achieved. (29, 30, 337)

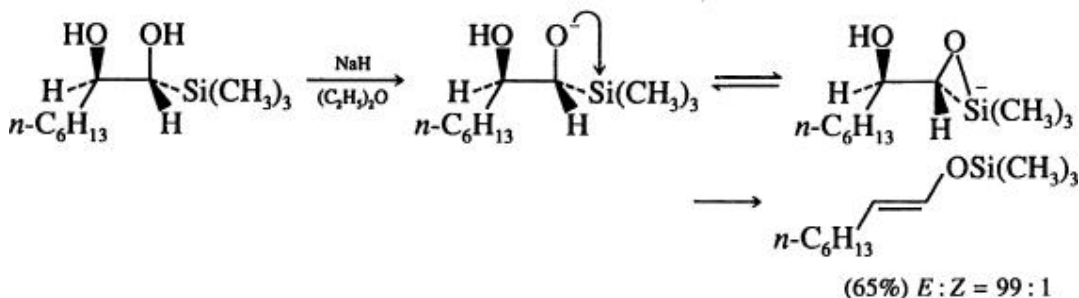


The mechanism outlined in Eq. 27 has gained wide acceptance since it is analogous to the acid-catalyzed pathway for a Peterson-type elimination.

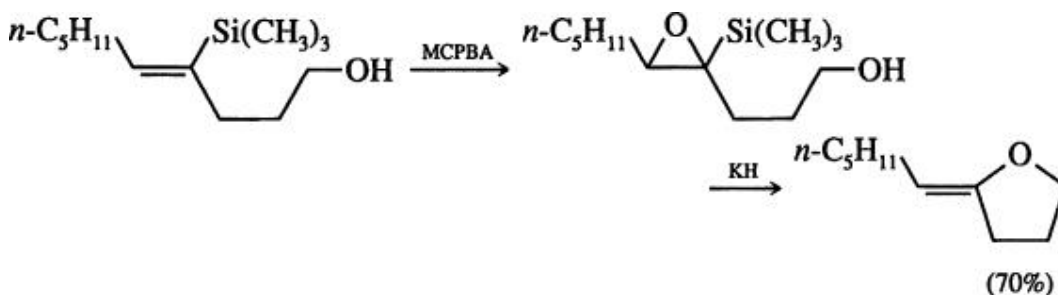
However, this mechanism may not be correct. Treatment of diol **169** with trifluoroacetic acid gives rise to aldehyde **170** as detected by NMR. Protodesilylation is achieved by a protic acid. Thus, the reaction pathway may be similar to the pinacol rearrangement and involve a 1,2-silicon migration. (338)



Treatment of a dihydroxysilane with base results in elimination through both α - and β -oxidosilanes unless the base is sodium hydride in diethyl ether. In this case, the reaction is highly stereospecific and *anti* elimination is observed. (53)

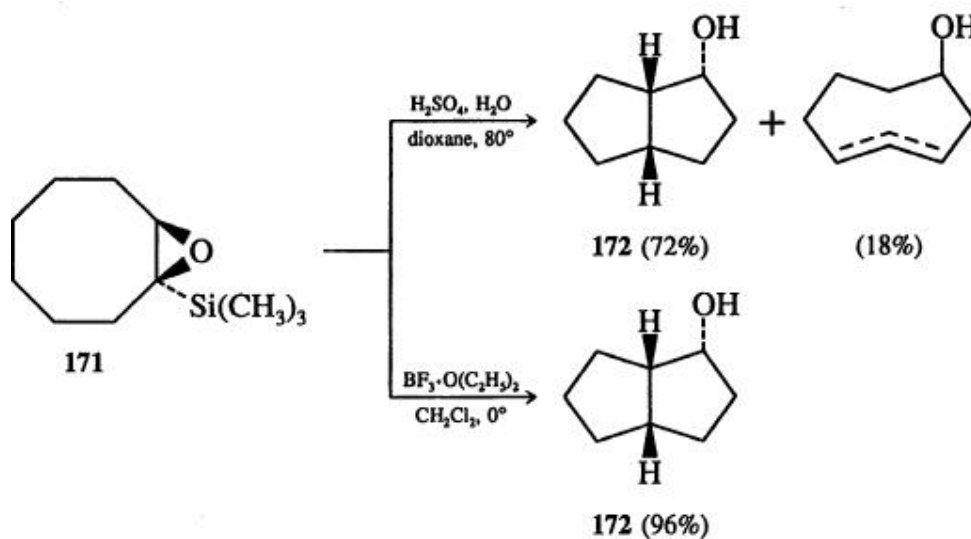


An α , β -epoxysilane can be opened in an intramolecular manner within the appropriate system. (339)

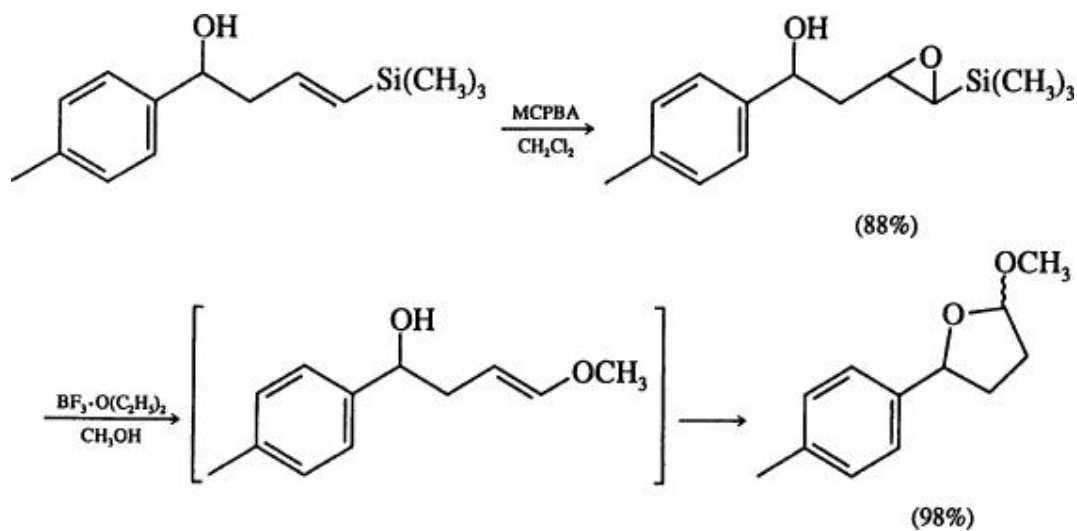


In medium-sized rings, transannular interactions can play a significant role, particularly if aprotic conditions are employed.

1,2-Epoxy-1-trimethylsilylcyclooctane (**171**) gives three products when treated with sulfuric acid, but the bicyclo[3.3.0]octane derivative **172** is formed exclusively with boron trifluoride. (31)



A method derived from the hydrolysis of α, β -epoxysilanes provides a route to O-methylactols. (174)



The presence of an α -silyl group allows an allyl alcohol to be epoxidized stereoselectively, (340) but subsequent treatment with a Lewis acid can

provide a mixture of products, depending upon the exact nature of the system. (341, 342)

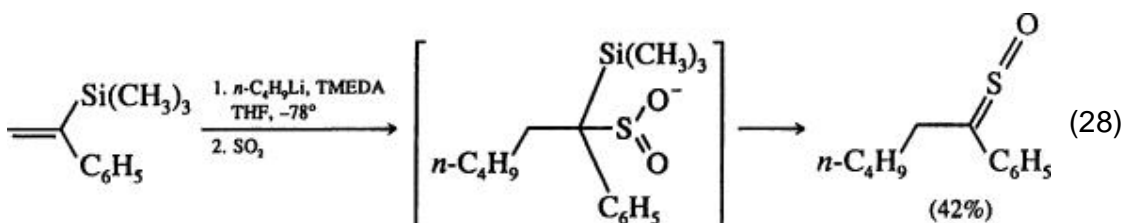
3.4. Related Reactions

3.4.1.1. Other Electrophiles

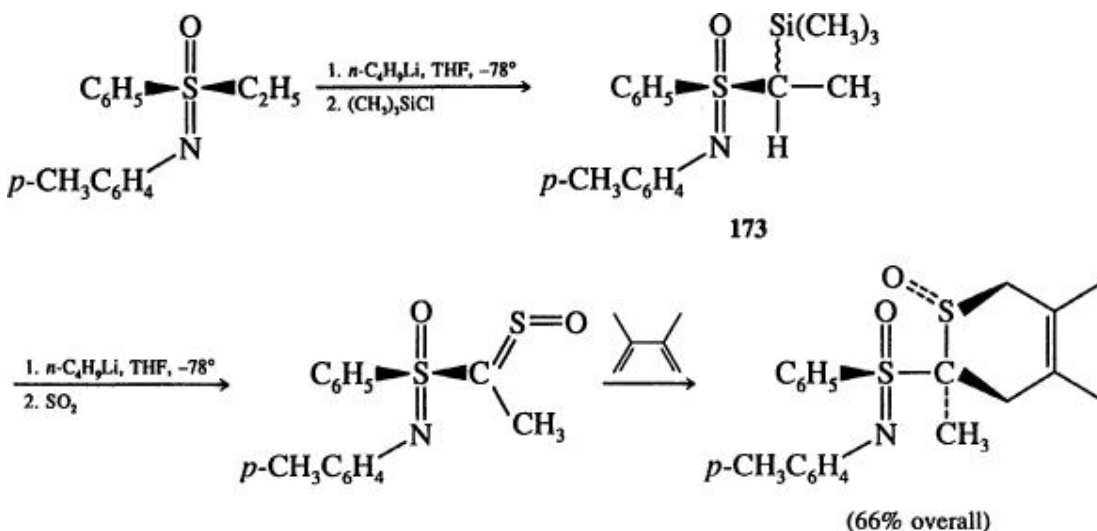
In addition to carbonyl compounds, other electrophiles condense with α -silyl carbanions and result in the formation of a double bond through elimination of the elements of a silanoxide.

3.4.1.1.1. Sulfur Dioxide (342)

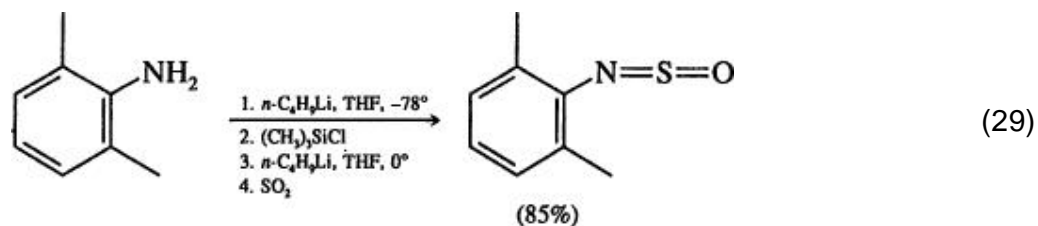
Sulfur dioxide serves as a good electrophile for α -silyl carbanions, and elimination occurs spontaneously to provide an excellent method for the preparation of sulfines. The α -silyl carbanions are, of course, available by the usual methods, such as direct deprotonation of a silane (343, 344) or addition of an alkyllithium to a vinylsilane. (128)



This method is useful for the preparation of chiral sulfines; the silane 173 need not be isolated. (345)

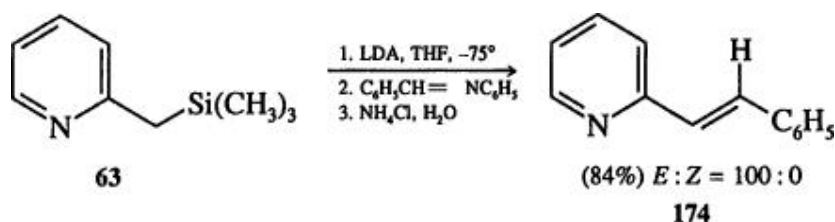


The use of *N*-silylamines allows the preparation of *N*-sulfinylamines, although excess sulfur dioxide is required to minimize diimine formation. (227)

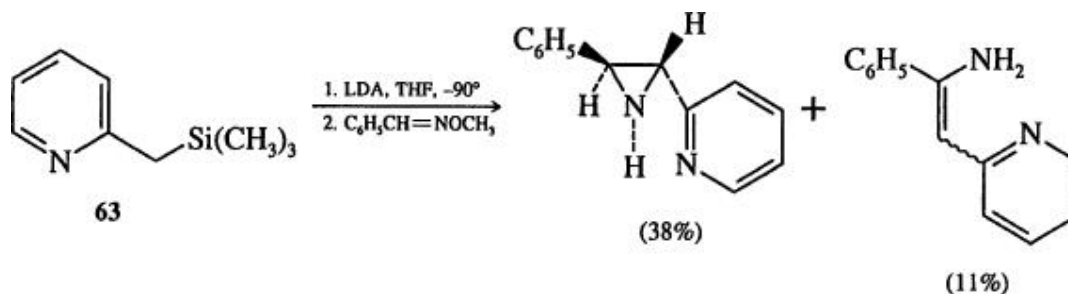


3.4.1.1.2. Nitrogen-based Electrophiles

α -Silyl carbanions condense with imines to yield alkenes. (346) The best results are obtained with imines derived from aryl aldehydes, and stereoselectivity is excellent.

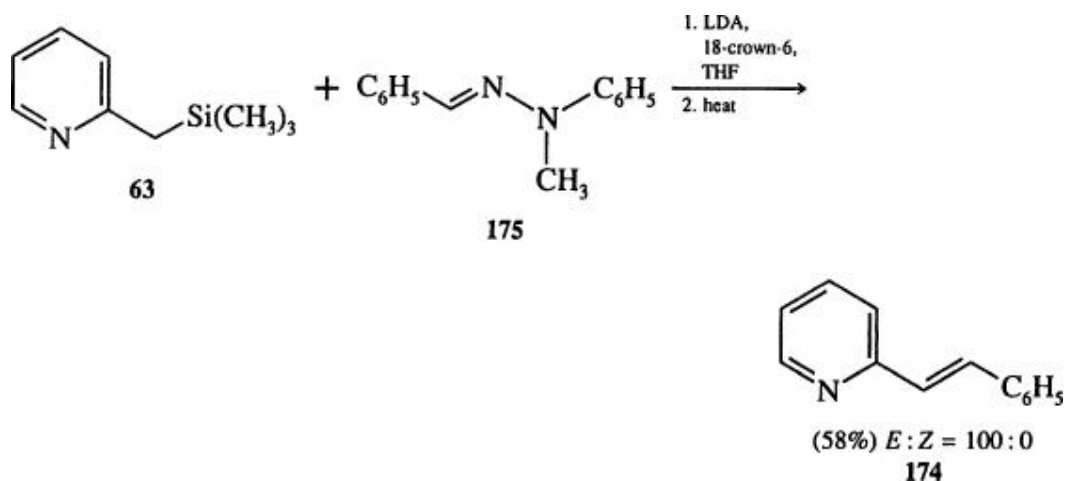


With an oxime ether as electrophile, a mixture of aziridine and enamine is produced. (347)

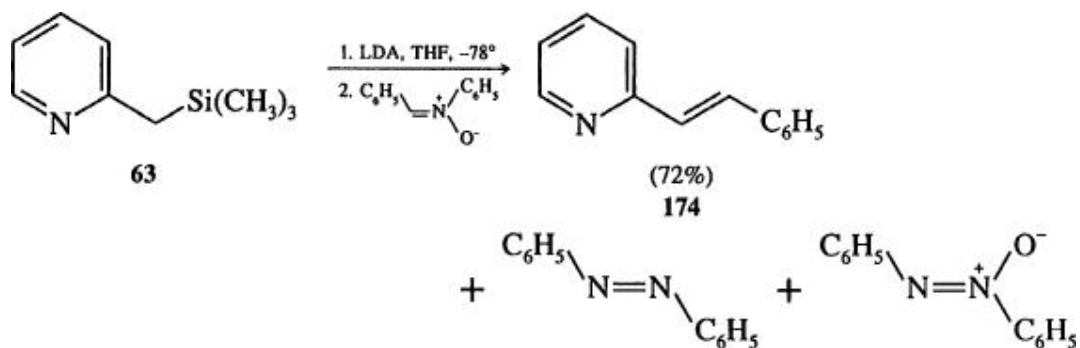


The hydrazone 175 also gives the alkene 174, but forcing conditions are required to achieve this reaction. The condensation fails if the monosubstituted

amine is used rather than the *N*-methyl compound. In the presence of [2.2.1]-cryptand, an agent that forms a complex with lithium, the reaction proceeds at low temperature, albeit in low yield, to give the *Z* product. As the *E* isomer is the product formed without these constraints, the reasons for the high stereochemical control are not clear. One explanation is that the *Z* isomer is the kinetic product while the *E* isomer is thermodynamically favored. (348)

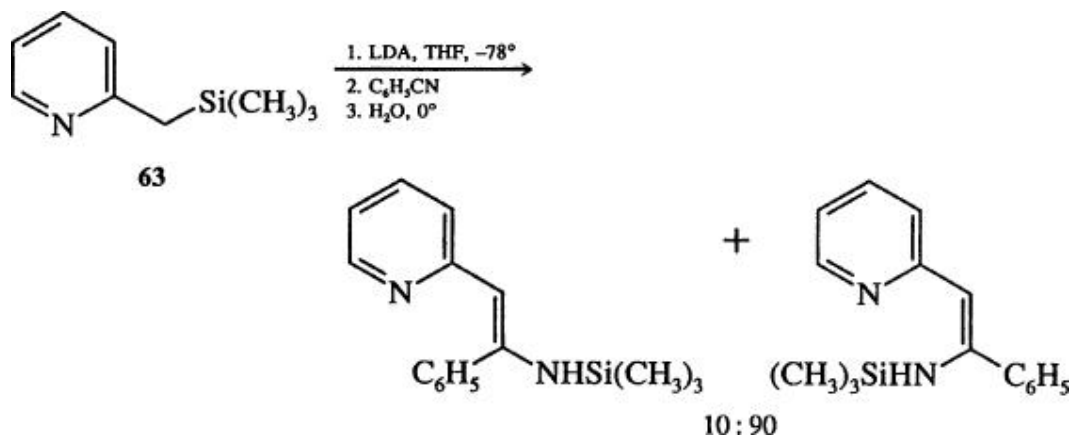


The analogous reaction with α -aryl-*N*-phenylnitrones gives a mixture of the *E* alkene **174**, azobenzene, and azoxybenzene. (349) If a cyclic nitron is

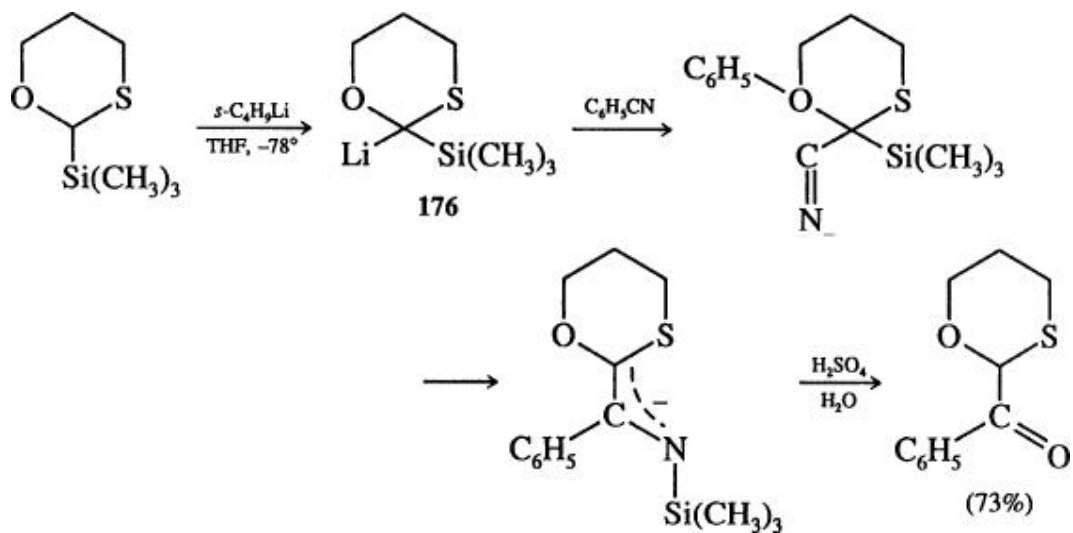


used as the electrophile, then aziridines and hydroxylamine derivatives can also be formed. (349, 350)

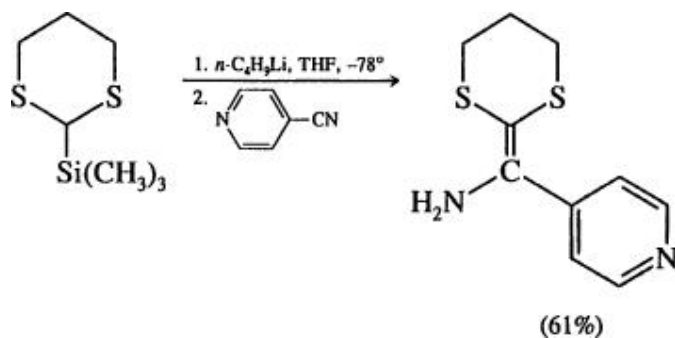
When benzonitrile is the electrophile, an enamine results whose geometry is dependent upon the reaction conditions. (351, 352)



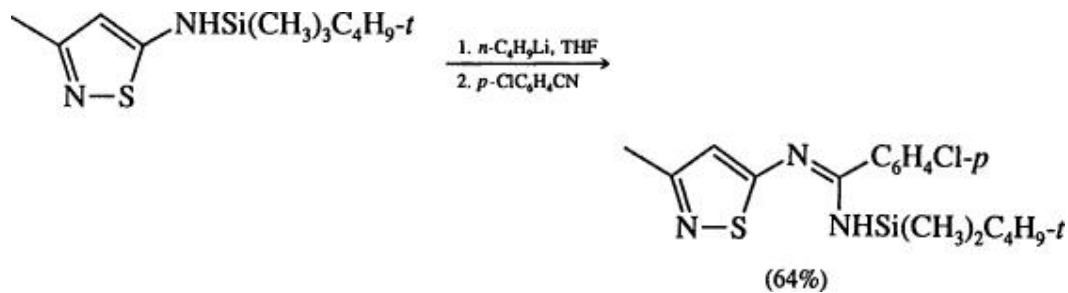
Condensation of 2-lithio-2-trimethylsilyl-1,3-oxathiane (**176**) with benzonitrile results in a silicon transfer from carbon to nitrogen to yield an enamine anion which affords the carbonyl compound on aqueous acid workup. ([320](#), [353](#)) This methodology has been extended for the preparation of 1,3-dithiane aminoketene



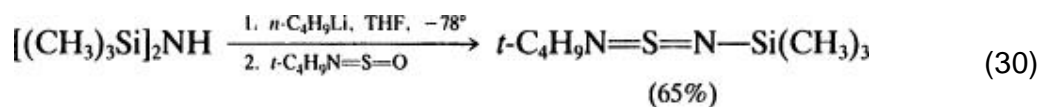
thioacetals ([354](#)) and isothiazole derivatives. ([355](#)) The silicon is not necessary for these reactions to proceed.



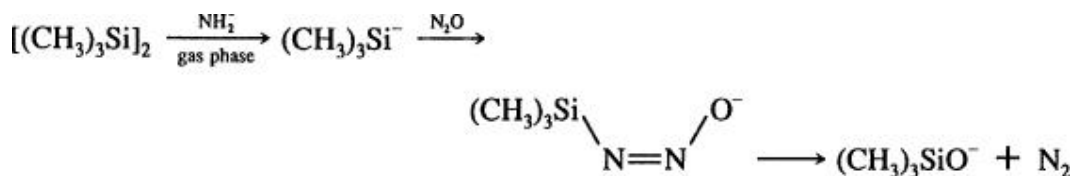
In addition to carbon electrophiles, *N*-silyl reagents undergo a Peterson olefination reaction with nitriles to afford silylimines. (355)



N-Silyl anions react with sulfinylamines to yield thiodiimide. (356) The reaction analogous to Eq. 30 with an isocyanate gives the carbodiimide (56%). (356)

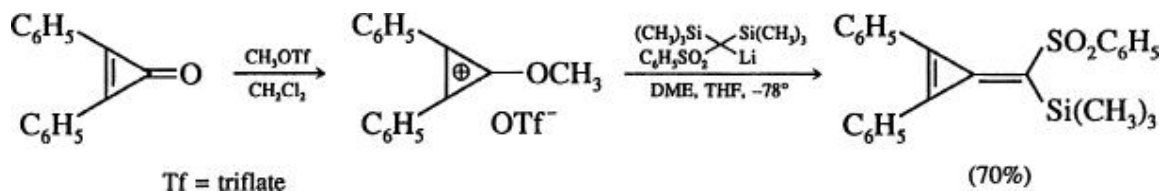


Reaction of a trimethylsilyl anion with nitrous oxide in the gas phase involves nucleophilic attack at the terminal nitrogen atom; this adduct then collapses by a Peterson-type reaction. (357)



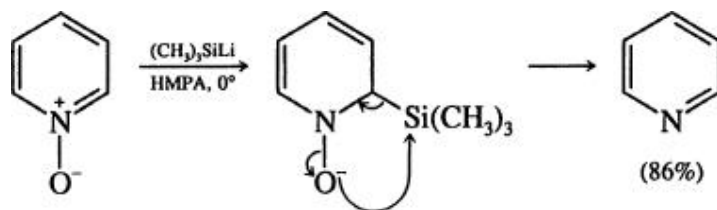
3.4.1.1.3. Cyclopropylium Ions

This class of compounds provides a useful method for the synthesis of substituted trifulvenes. (358)



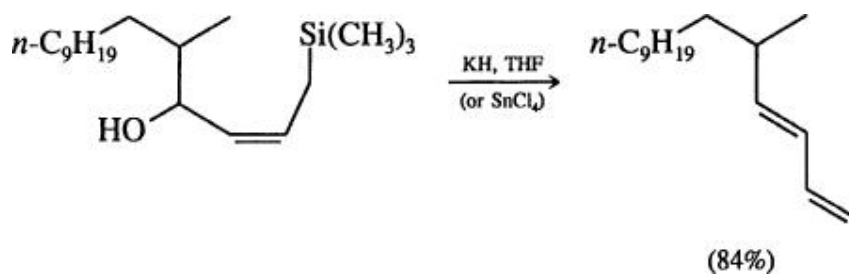
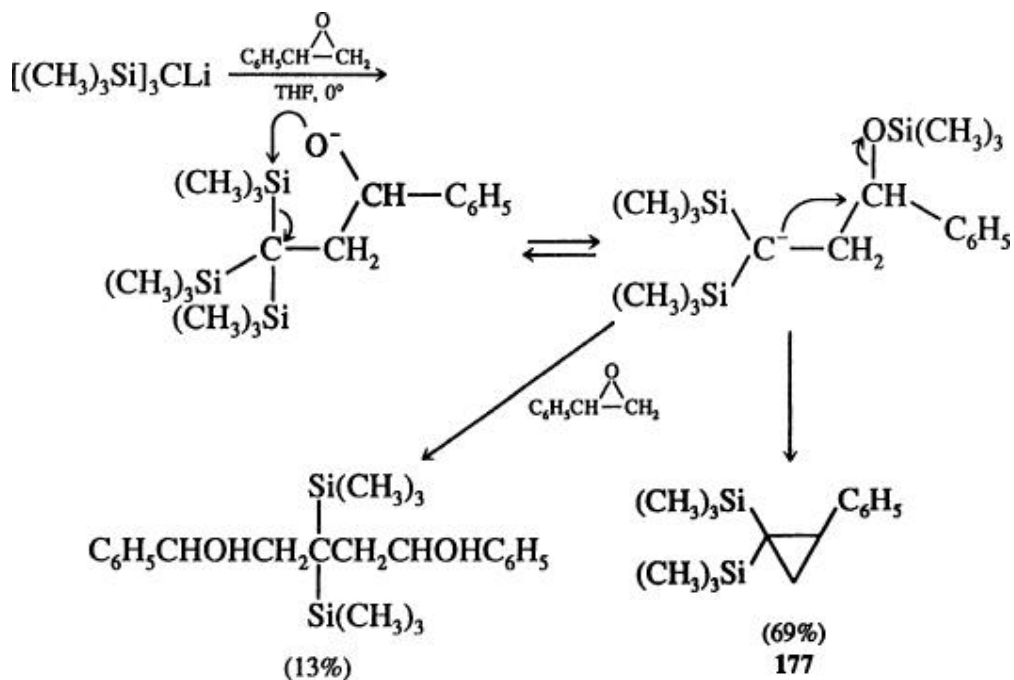
3.4.1.1.4. Deoxygenation of Pyridine N-Oxide

The deoxygenation of pyridine *N*-oxide by trimethylsilyllithium, generated in situ from hexamethyldisilane, could involve a Peterson-type elimination. (359)



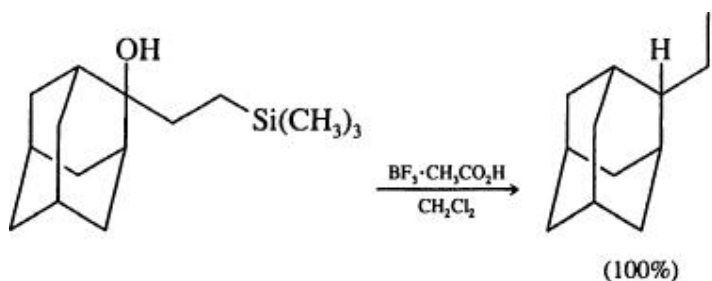
3.4.1.2. The Homo-Peterson Reaction

The Peterson olefination reaction necessitates interactions between oxygen and silicon atoms situated on adjacent carbon atoms. Reactions also occur when the two heteroatoms are separated by three carbon or another element's atoms, but the intermediate carbanion must be stabilized. Reaction of tris(trimethylsilyl)methyl lithium with styrene oxide gives cyclopropane **177** in good yield. (163, 325, 360) The spacer between the oxygen and silicon atoms can be even larger. (361)

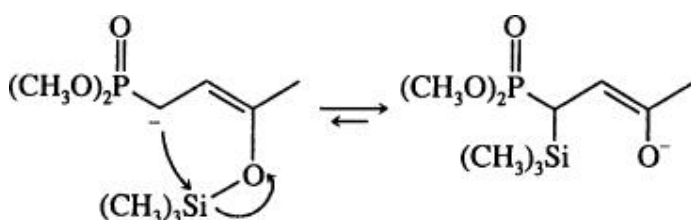


The overall philosophy is related to an approach to *o*-quinodimethanes, but as the reaction involves nucleophilic attack at a silyl group by an external nucleophile and loss of a remote leaving group, it is not a descendant of the homo-Peterson reaction. (361-364) This is also true for the conversion of γ -hydroxysilanes to alkenes by Lewis acids, which no doubt proceeds by way of an allylsilane and protodesilylation. (365)

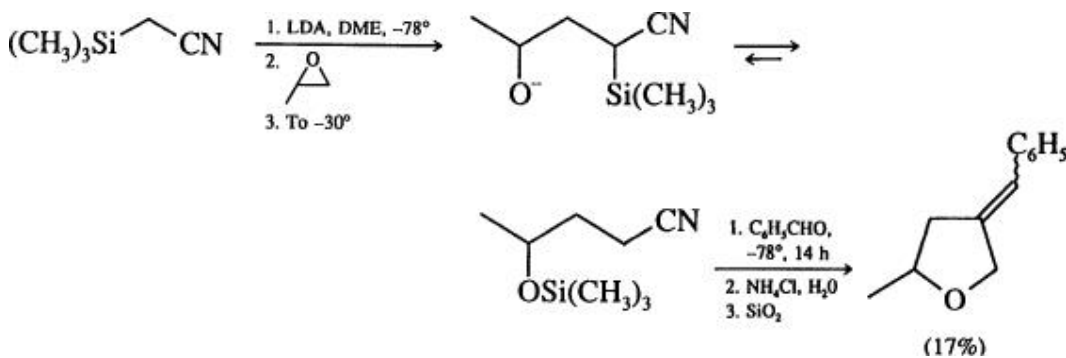
Many reactions can be related to a homo-Peterson reaction by virtue of a



1,3 transfer of a silyl group, (366) such as for the reaction of an O-silylketene acetal with a carbonyl compound, (13, 367) and sigmatropic rearrangements. (368) The relationship stops at this stage because subsequent elimination would be thermodynamically unfavorable; (368) the anions formed in such a rearrangement

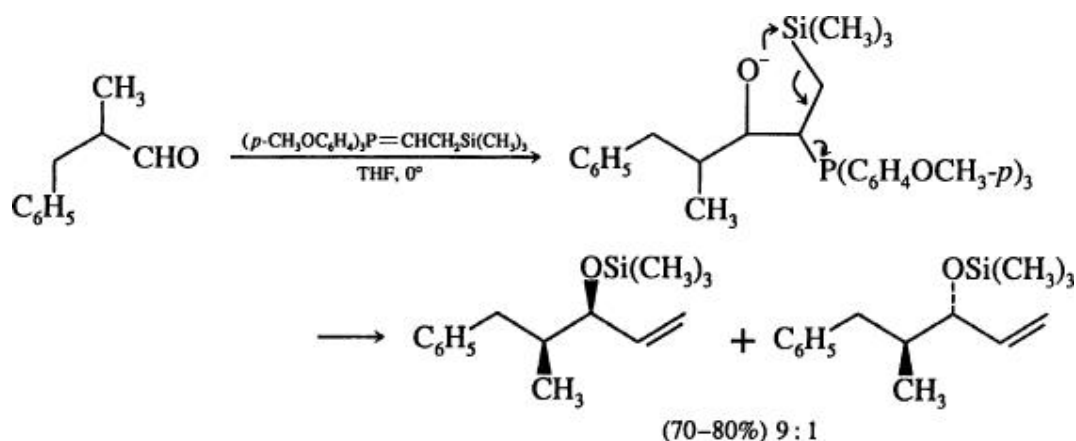


can, however, be used in further reactions (369) or provide an elegant method

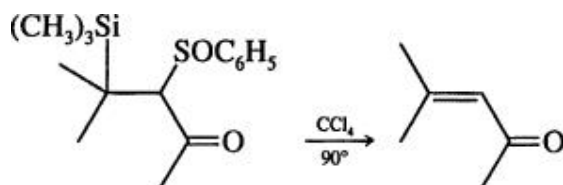


for the removal of the silyl group once it has done its job directing, for example, the stereochemistry of an addition. (318, 370-373)

Under very special conditions, an α, ω -silicon shift can be thermodynamically favorable. One example is used for the preparation of allyl alcohols. (374)



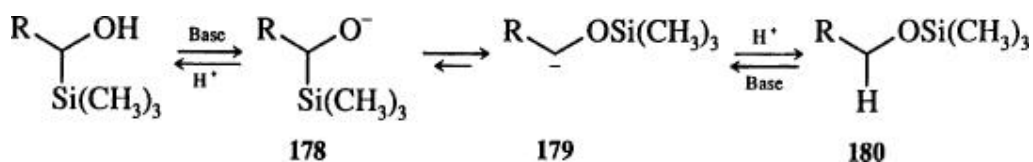
Although the elimination of β -silyl sulfoxides can be considered a homo-Peterson analog, the requirements of this elimination suggest that the silyl group is acting as a bulky proton equivalent. (375-377) Indeed, there are many



reactions for the formation of alkenes by elimination from the $=\text{Si}-\text{C}-\text{C}-\text{X}$ system, where the silicon acts as a proton equivalent to an external nucleophile, and X is a leaving group. (378-380)

3.4.1.3. The Brook Rearrangement and Related Reactions (381-383)

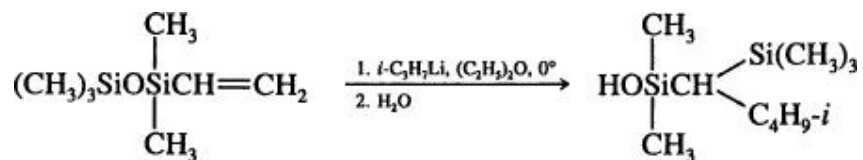
α -Hydroxysilanes can undergo a rearrangement after deprotonation. The product, or product mixture, depends upon the relative stabilities of the two anions **178** and **179**. This reaction, which is only indirectly related to the Peterson reaction,



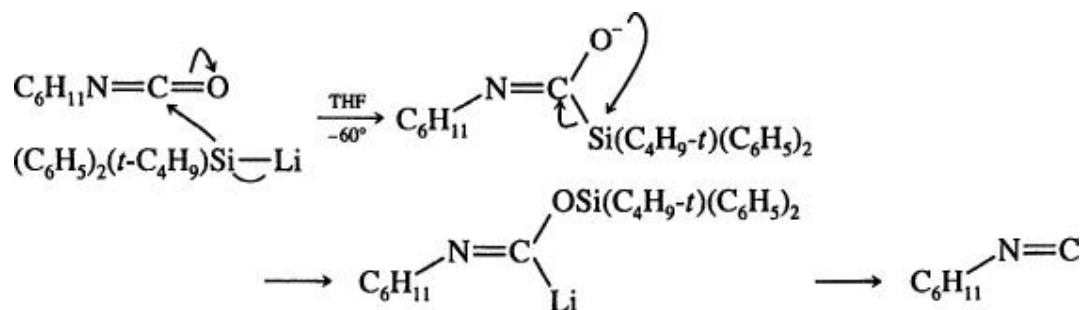
has enjoyed considerable usage in synthetic methodology. (384-389) The reverse reaction, conversion of a silyl enol ether into an α -hydroxysilane, can be accomplished by a strong base. (390-393) Analogous rearrangements of a silyl group from sulfur to carbon (394) and from oxygen to nitrogen (395) also

proceed.

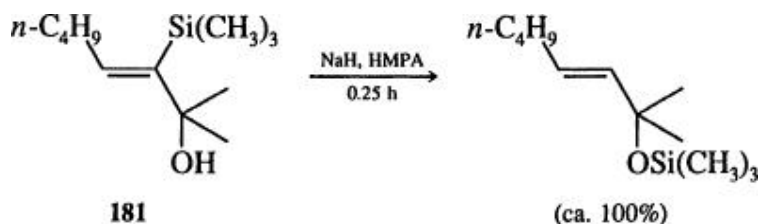
A reaction similar to the Brook rearrangement is observed when vinyldisiloxanes are reacted with an alkyllithium. (396)



A further variant of the rearrangement is observed for the deoxygenation of isocyanates with *tert*-butyldiphenylsilyllithium. The mechanism was elucidated by NMR studies. (397, 398)

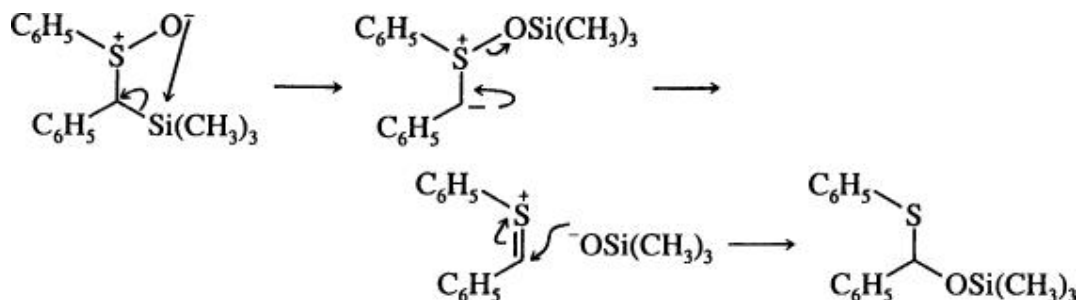


A 1,3-silicon migration is observed when β -hydroxyvinylsilanes **181** are treated with a catalytic amount of sodium or potassium hydride in HMPA. (399, 400) The mechanism of this reaction is not clear, but probably involves a four-center intramolecular transition state, although an intermolecular pathway has not been excluded experimentally.



3.4.1.4. The Sila-Pummerer Rearrangement

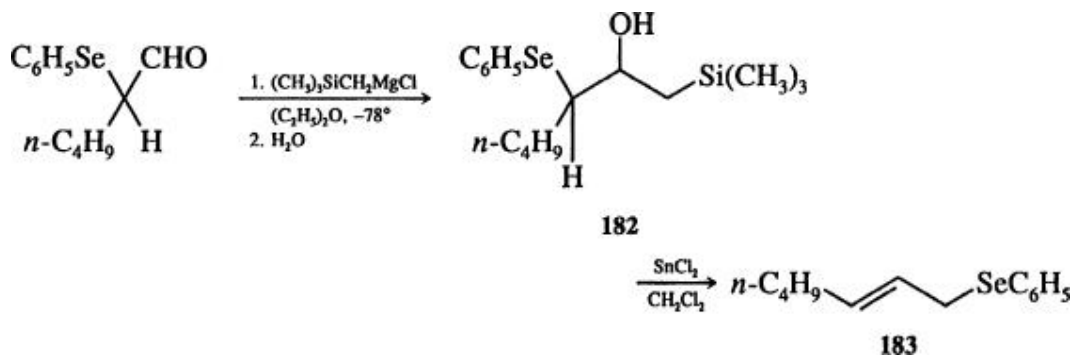
In many respects, this rearrangement is closely related to Peterson-type transformations because a silyl group is transferred from carbon to oxygen, followed by expulsion of the silanoxide moiety, which can then react further with the resultant sulfur ylide. The last



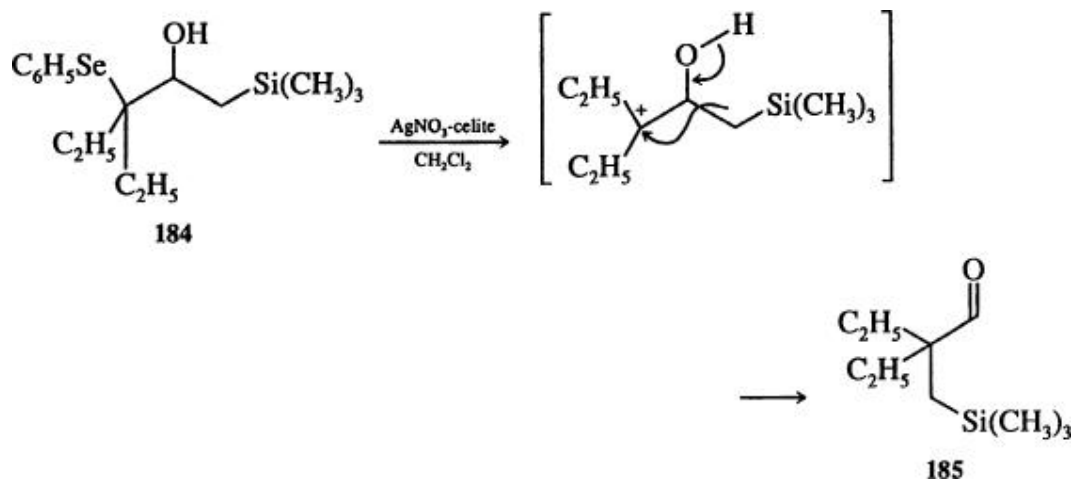
part of the reaction is susceptible to stereoelectronic effects, and the sulfur ylide can lose a proton to afford a vinyl sulfide as a competing reaction pathway. (16, 148, 150, 153, 401-407) The analogous reaction has been observed for α -silyl selenides, although it is not as clean as in the sulfur series. (408-411)

3.4.1.5. Other Reactions

Reactions of the β -hydroxysilane **182**, obtained from the α -selenoselenide, with tin(II) chloride results in formation of the allyl-selenide **183** through selenium migration. However, treatment of alcohol **184**

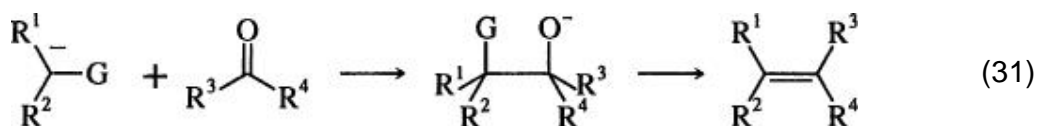


with silver nitrate results in the β -silyl aldehyde **185**; treatment with tin(II) results in a mixture of aldehyde **185** and the corresponding allylselenide. (412)



4. Comparison with Related Reactions

The Peterson olefination reaction is a member of a general class of transformations which provide an alkene by condensation of a functionalized carbanion with a carbonyl compound, followed by elimination of the oxygen and functional group. (413) The best-known reaction of this type is the Wittig reaction ($G = {}^+PR_3$), (414-418) together with its variants. (419) Other elements that have been used for the elimination described in Eq. 31 are: aluminum ($G = AlR_2$), (420)

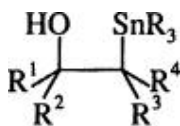


antimony ($G = SbR_2$), (421) arsenic ($G = AsR_2$), (417, 422, 423) boron ($G = BR_2$), (424, 425) lead ($G = PbR$), (421, 426) magnesium ($G = MgR$), (427) mercury ($G = HgR$), (428, 429) selenium ($G = SeR$), (430) tellurium ($G = TeR$), (431, 432) tin ($G = SnR_3$), (433) zinc ($G = ZnR$), (434) and sulfur as sulfides, (435) sulfoxides, (436-438) sulfinamides, (439, 440) and sulfones. (249, 441) Many of these eliminations require special conditions or the change of oxidation level, as with sulfones.

Despite the proliferation of elements, the only examples that have enjoyed widespread usage and compete with the Peterson protocol are those of organotin and organophosphorus compounds.

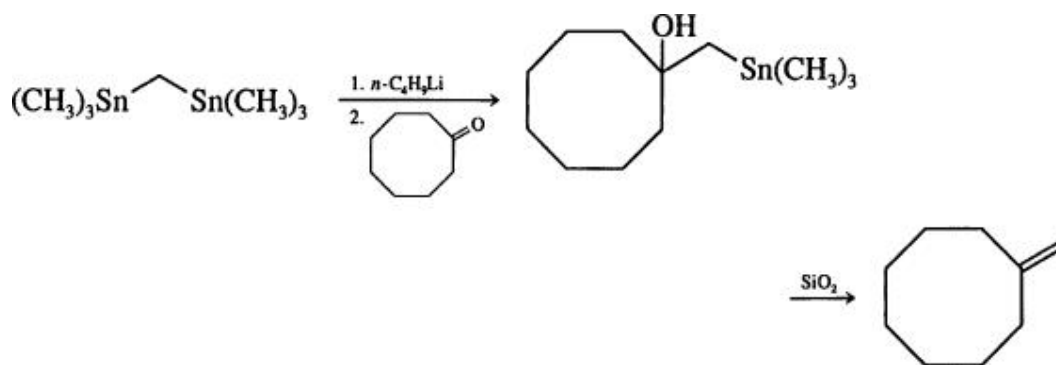
4.1.1.1. Organotin Compounds

Tin is in the same period as silicon and therefore deserves special mention. β -Hydroxystannanes **186** are prepared by methods similar to those used for organosilanes. For example, an epoxide is opened by triphenylstannyl alkali metals, (426) while carbonyl compounds condense with trialkylstannylmethyl lithium. (442-444) In general, elimination from a β -hydroxysilane



186

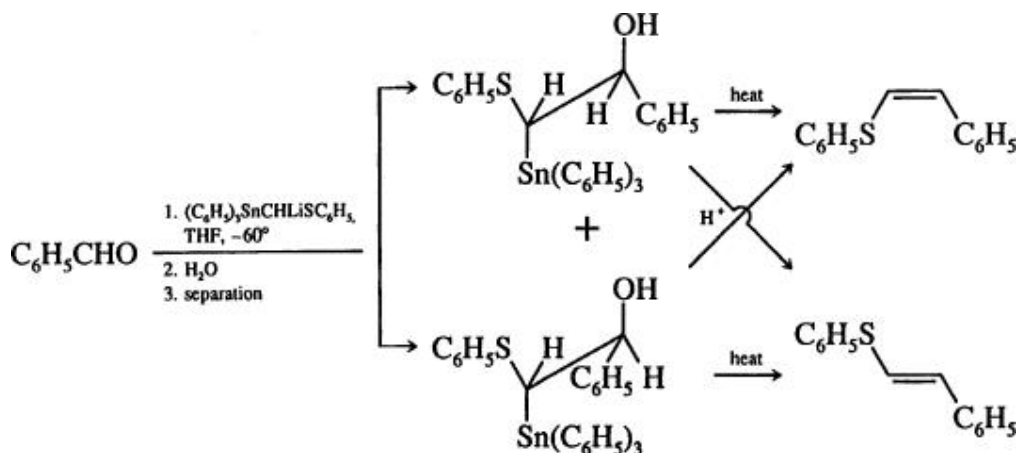
186 requires a potassium counterion, rather than lithium, or acidic conditions. More vigorous conditions (perchloric acid) are required for triphenylstannyl



derivatives of **186** than for the trimethylstannyl series which eliminate on silica. (442) Other electrophiles, such as esters which provide ketone enolates through tin elimination from the intermediate α -stannylketone (445) and α -chloroketones, (442) also react with α -stannylcarbanions.

When other anion-stabilizing groups are present in conjugation with α -stannylcarbanions, alkene formation is facilitated and the intermediate β -hydroxystannane need not be isolated. (313-445a) The stereochemistry of this elimination is analogous to the Peterson olefination reaction: *anti* elimination is observed under acidic conditions, while the *syn* pathway is followed for thermolytic, and presumably basic, conditions. (446)

At present, the methodology for the formation of alkenes from β -hydroxystannanes is still under development. As cited above, the eliminations are facile, but the high formula weight of the stannyl moiety, particularly if tri-*n*-butylstannyl is employed, coupled with the additional separation of the nonvolatile tin byproduct, detract from the use of this protocol. In addition, when the tin is juxtaposed to an electron-withdrawing group, purification of



the stannane can be problematic. (260) In many systems the choice of base to effect formation of the α -stannyl carbanion is limited to lithium amides in order to avoid transmetalation.

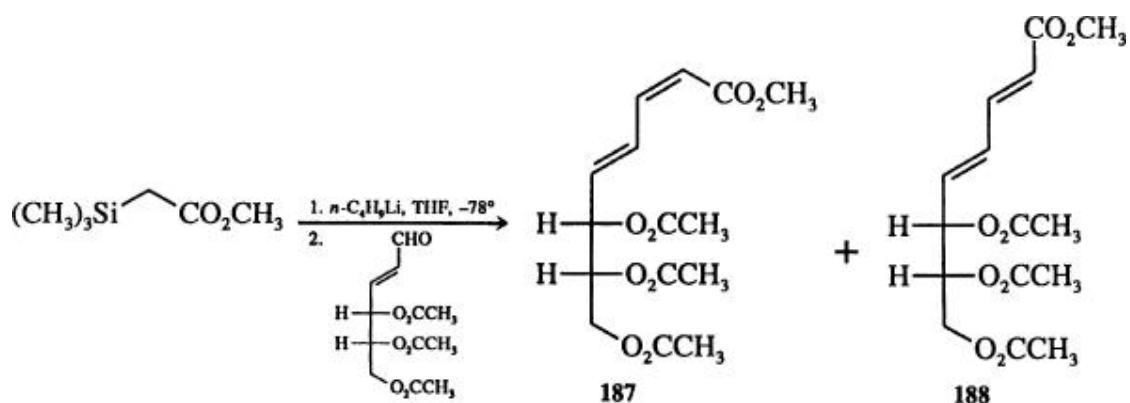
4.1.1.2. Wittig Reaction

The Peterson olefination reaction usually gives rise to hexamethyldisiloxane as the byproduct, which because of its low boiling point (100°) is easily removed when the reaction or extraction solvent is evaporated. In contrast, the byproduct of the Wittig reaction is triphenylphosphine oxide, which on occasions can be troublesome to remove; use of phosphonate derivatives can alleviate this problem.

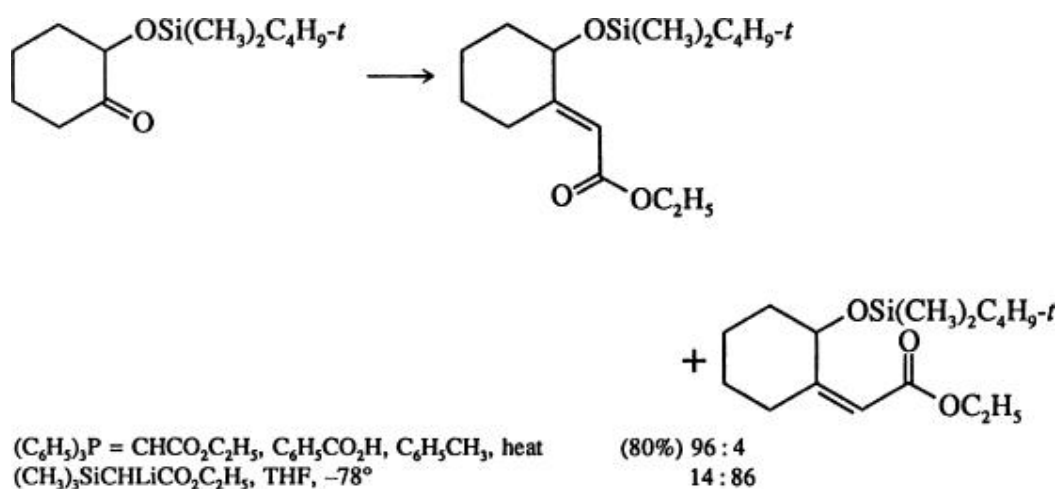
The stereochemical outcome of the Peterson reaction, when only alkyl substituents are present, may be controlled with certainty, although separation of the diastereomeric β -hydroxysilanes may be necessary. Such a separation is not required to control the stereochemical outcome of the Wittig reaction; the major isomer is dependent on the reaction conditions. A variety of models have been proposed to rationalize and predict the alkene stereoselectivity from a phosphorus ylide. (416, 447-449) These arguments were based on a rationale derived from the observed *E:Z* ratios, but the intermediate can be observed by NMR techniques. (450) Thus the reaction outcome can be predicted with certainty. (451, 452)

When an electron-withdrawing group is present on the same carbon atom as the phosphorus moiety, the Wittig reaction usually provides the *E* alkene as the major product. (416) The stereochemical outcome of the analogous Peterson reaction can be controlled. In many cases, however, poor stereochemical control is observed. This property can be exploited. Peterson methodology provides the *E,Z* dienic ester **187** in a 1:1 mixture with the *E,E* isomer **188**. (205, 453) The Wittig protocol gives a 35:65 mixture of **187** and **188**, at best. Thus the silicon method is the route of choice for the preparation of the *E,Z* ester **187**.

When a heteroatom is present in the carbonyl moiety, chelation-controlled condensation occurs, which in turn leads to stereoselectivity. (50, 84) In some cases,



the corresponding Wittig approach can show poor selectivity, (50) or give the opposite selectivity. (84)



An additional advantage of the Peterson olefination over the Wittig reaction occurs when an electron-withdrawing group is present, in that the α -silyl carbanion condenses with carbonyl compounds and undergoes elimination of the silicon moiety rapidly (within minutes). The corresponding reaction with a stabilized phosphorus ylide is often extremely slow.

Finally, the Peterson reaction can proceed when a Wittig reaction fails as a consequence of less steric constraints preventing attack of the ylide on the carbonyl group (see Eq. 15).

The choice between use of a phosphorus or silicon reagent depends on the compound required as product. If the general reaction requirements include a rapid reaction with a stabilized carbanion, the formation of a thermodynamically less-stable isomer of a functionalized alkene, a simple

separation procedure for byproducts, or methylenation of a hindered carbonyl group, the elimination of a silicon group would prove advantageous.

In contrast, stereochemical control for the preparation of hydrocarbon alkenes and the thermodynamically most stable isomer of functionalized alkenes, the availability of the phosphorus precursors, and the greater anion-stabilizing properties of this element which facilitates carbanion formation, often give a Wittig variant a strategic advantage. All of these variations are noted throughout this chapter. Unfortunately, it is not possible to generalize which element, phosphorus or silicon, is most advantageous. Each case must be considered on its own merits (e.g., whether the α , β -unsaturated ester **187** or **188** is the required product). As illustrated in this chapter and its accompanying tables, the Peterson olefination reaction can have distinct advantages over the Wittig reaction under certain constraints, and in some cases the two approaches are complementary.

5. Experimental Conditions

The experimental conditions for the majority of Peterson olefination reactions require condensation of a carbanion, derived from a silane, with a carbonyl compound. Formation of this carbanion invariably involves use of a strong base, such as *n*-butyllithium or lithium diisopropylamide, in an ethereal solvent. Reactions must therefore be performed under an inert atmosphere (nitrogen or argon). The most commonly used solvents are tetrahydrofuran, diethyl ether, and 1,2-dimethoxyethane. To obtain optimum yields, these solvents should be freshly distilled from lithium aluminum hydride or sodium–benzophenone.

When the α -silyl carbanion contains other α -functional groups, the substituted alkene is usually generated under the conditions used for the condensation step, and no special precautions are necessary during workup. In the absence of any anion-stabilizing moieties, the β -hydroxysilane can be isolated. To alleviate any problem of premature elimination, strongly acidic or basic conditions must be avoided during this isolation procedure.

6. Experimental Procedures

The procedures presented here have been chosen to illustrate the application of the Peterson olefination reaction for the preparation of a wide variety of both functionalized and nonfunctionalized alkenes. General procedures for the elimination of β -hydroxysilanes have also been included for solely alkyl-substituted examples.

As the success of this synthetic protocol for the formation of olefins relies upon the availability of an appropriately substituted silane, illustrative examples of the preparation of this latter class of compounds are included in this section. Although the preparation of 5-trimethylsilyl-4-octanol is accomplished by reduction of a carbonyl precursor rather than a Peterson protocol, the first four procedures are included to illustrate the problems associated with a stereospecific β -hydroxysilane synthesis.

Unless stated otherwise, the reaction procedures outlined below can be performed in the appropriate size three-necked, round-bottomed flask fitted with a dropping funnel, nitrogen inlet, serum stopper, thermometer, and magnetic stirrer bar. Reagents can be added by syringe through the serum stopper.

6.1.1. 5-Trimethylsilyl-4-octanol (Preparation of a β -Hydroxysilane) (27)

6.1.1.1. 2-Trimethylsilylvaleric Acid

A solution of vinyltrimethylsilane (1.0378 g, 10.35 mmol) in tetrahydrofuran (50 mL) was cooled to -78° , and a solution of ethyllithium (8.25 mL of a 1.63 M solution in ether, 13.4 mmol) added. The reaction mixture was stirred at -78° for 10 hours, warmed to 0° for 1 hour, and then cooled again to -78° . The mixture was then added to excess crushed dry ice in pentane. As soon as the excess solid carbon dioxide had evaporated, the resultant mixture was added to cold 6 M hydrochloric acid, forming a slurry containing ice. When the ice had melted, the mixture was shaken in a separatory funnel, and the organic layer separated, dried (MgSO_4), concentrated, and evaporatively distilled (oven temperature 150°) to give 2-trimethylsilylvaleric acid (1.515 g, 84%) as a liquid which solidified below room temperature; IR (film) 3570–2500, 1690, 1250, 850 cm^{-1} ; ^1H NMR (CCl_4) δ 0.00 (2H, s, impurity), 0.10 (9H, s), 0.8–1.1 (3H, br), 1.1–1.8 (5H, br), 1.8–2.1 (1H, m).

6.1.1.2. 5-Trimethylsilyl-4-octanone

Oxalyl chloride (0.58 mL, 0.86 g, 6.8 mmol) was added to a solution of 2-trimethylsilylvaleric acid (0.396 g, 2.27 mmol) in hexane (15 mL), the reaction mixture being protected from the atmosphere by a drying tube. The mixture was stirred for 2 hours at ambient temperature, then placed under aspirator vacuum to give the crude acid chloride which was used in the

following reaction sequence without further purification.

A mixture of copper(I) iodide (1.30 g, 6.8 mmol) and diethyl ether (10 mL) was cooled to 0°, and a solution of *n*-propyllithium (11.2 mL of a 1.23 M solution in diethyl ether, 13.8 mmol) was added. After stirring for 15 minutes, the reaction mixture was cooled to -78°, taken up in a syringe, and then added to a solution of the above acid chloride in diethyl ether (15 mL) which was also cooled to -78°. The resultant mixture was stirred for 1 hour at -78°, for 1 hour with warming to 0°, and for 30 minutes at 0°; then the mixture was poured into 10% aqueous ammonium chloride solution overlaid with diethyl ether. The organic layer was separated, dried (MgSO₄), concentrated and evaporatively distilled (oven temperature 150°) to give 5-trimethylsilyl-4-octanone (0.293 g, 64%); IR (film) 2940, 1690, 1250, 840 cm⁻¹; ¹H NMR (CHCl₃) δ 0.00 (9H, s), 0.7–1.9 (14.5H, br), 2.0–2.5 (3H, m).

6.1.1.1.3. 5-Trimethylsilyl-4-octanol

Diisobutylaluminum hydride (26.2 mL of a 0.96 M solution in hexane, 25.2 mmol) and pentane (10 mL) were placed in one side of a two-bottomed flask; in the other side of the flask were placed 5-trimethylsilyl-4-octanone (1.679 g, 8.38 mmol) and pentane (20 mL). The flask was immersed in a liquid nitrogen–ethanol bath (-120°) for 1 hour to allow the temperature to equilibrate. The flask was then tipped to mix the contents. The resultant mixture was kept at -120° for 3 hours, and then warmed slowly to -20° overnight. The mixture was poured into 2 M hydrochloric acid overlaid with ether. The organic layer was washed with saturated aqueous sodium hydrogen carbonate solution, dried (MgSO₄), concentrated, and evaporatively distilled (oven temperature 160°) to give the β-hydroxysilane (1.6540 g, 98%); IR (film) 3450, 2940, 1250, 840 cm⁻¹; ¹H NMR (CHCl₃) δ 0.00 (9H, s), 0.7–1.1 (7H, br), 1.1–1.8 (10H, br), 2.1–2.4 (1H, m), 3.85 (1.4H, br).

6.1.1.1.4. 5-Trimethylsilyl-4-octanol (Alternative)

A solution of vinyltrimethylsilane (0.679 g, 6.77 mmol) in tetrahydrofuran (10 mL) was cooled to -78°, and ethyllithium (7.65 mL of a 1.15 M solution in diethyl ether, 8.8 mmol) was added. The mixture was stirred for 2 hours at -78°, warmed over 1 hour to -30°, and cooled again to -78°. *n*-Butyraldehyde (0.66 mL, 0.54 g, 7.5 mmol) was added, and the reaction mixture warmed to room temperature over 1 hour, and then stirred for an additional 2 hours. The reaction mixture was poured into saturated aqueous sodium chloride solution overlaid with diethyl ether. The organic layer was separated, dried (MgSO₄), concentrated, and evaporatively distilled (oven temperature 120°) to give 5-trimethylsilyl-4-octanol (1.272 g, 93%), whose spectroscopic properties are given above.

6.1.1.2. Elimination of 5-Trimethylsilyl-4-octanol with Potassium Hydride in Tetrahydrofuran (27)

Potassium hydride (0.10 g of a 50% slurry in oil, ca. 1.25 mmol) was stirred with pentane (4 mL), and the liquid removed by pipet. To the residue was added a solution of 5-trimethylsilyl-4-octanol (76.5 mg, 0.378 mmol), prepared by the reductive methodology outlined above in tetrahydrofuran (5 mL) and *n*-butylbenzene (98.8 mg, internal standard for the VPC analysis). The mixture was stirred for 1 hour at ambient temperature and then added to cold 10% aqueous ammonium chloride overlaid with diethyl ether. The ethereal layer was separated, dried (MgSO₄), and analyzed by VPC showing a 5:95 ratio of (*Z*)- and (*E*)-4-octene formed in 96% yield.

6.1.1.3. Elimination of 5-Trimethylsilyl-4-octanol with Sodium Acetate in Acetic Acid (27)

5-Trimethylsilyl-4-octanol (98.1 mg, 0.485 mmol), prepared by the reductive method outlined above was added to glacial acetic acid (15 mL) saturated with sodium acetate at 50° together with *n*-butylbenzene (110 mg, internal standard for the VPC analysis). The reaction mixture was stirred at 50° for 30 minutes, cooled to room temperature, and poured into saturated sodium hydrogen carbonate solution overlaid with pentane. The organic layer was separated, washed with saturated aqueous sodium hydrogen carbonate solution, dried (MgSO₄), and analyzed by VPC showing a 98:2 ratio of (*Z*)- and (*E*)-4-octene formed in 85% yield.

6.1.2. Methyl 4,6-O-Benzylidene-3-deoxy-3-C-methylene- α -D-ribo-hexopyranoside (Reaction of Trimethylsilylmethylmagnesium Chloride) (454)

6.1.2.1.1. Methyl 2-O-Benzoyl-4,6-O-benzylidene-3-[(trimethylsilyl)methyl]- α -D-allopyranoside

Magnesium turnings (2.57 g, 106 mmol) were placed in a 1-L, three-necked flask equipped with a dry-ice condenser and equilibrating side-arm addition funnel. Serum stoppers were attached, the system flushed with argon, and flame dried. A flow of argon was passed through the apparatus for the duration of the experiment. Anhydrous diethyl ether (75 mL) and (bromomethyl)trimethylsilane (0.841 g, 5.0 mmol) were introduced. (Chloromethyl)trimethylsilane (14.2 g, 116 mmol) in diethyl ether (50 mL) was added dropwise at a rate sufficient to maintain a gentle rate of reflux. The mixture was stirred at reflux for an additional 1 hour. The apparatus was cooled and a solution of methyl 2-O-benzoyl-4,6-O-benzylidene- α -D-ribo-hexopyranosid-3-ulose (6.33 g, 16.5 mmol) in warm toluene (400 mL) was added dropwise. The solution was stirred for 3 hours, quenched with saturated aqueous ammonium chloride solution, and extracted with ether (1 L). The extracts were dried (MgSO₄) and evaporated to give the crude β -hydroxysilane as a syrup (8.85 g, 90%); ¹H NMR (CDCl₃) δ 0.10 (9H, s), 1.20 and 1.37 (2H, AB q), 3.40 (4H, s), 3.5–4.5 (4H, m), 4.88 and 5.10 (2H, AB q), 7.58 (1H, s), 7.1–7.6 (8H, m), 8.0–8.3 (2H, m).

6.1.2.1.2. Elimination with Potassium Hydride

The crude β -hydroxysilane was dissolved in anhydrous tetrahydrofuran (250 mL) and added carefully to a suspension of potassium hydride (8.5 g, 205 mmol) in tetrahydrofuran (225 mL). A reflux condenser was attached and the mixture heated under reflux for 4 hours. The opaque brown liquid was poured slowly into saturated aqueous ammonium chloride solution (300 mL) overlaid with diethyl ether (500 mL), and the layers separated. The aqueous layer was extracted twice with diethyl ether. The combined extracts were evaporated to give crude methyl 4,6-benzylidene-3-deoxy-3-C-methylene- α -D-ribo-hexopyranoside (3.9 g). Recrystallization from dichloromethane–hexane gave the pure alkene (2.71 g, 58%) in two crops; mp 194.5–195° and mp 188–189°; $[\alpha]_D^{20} + 145^\circ$.

6.1.2.2. Reaction of Trimethylsilylbenzyl Anion with Benzaldehyde (Direct Deprotonation) (91)

Methylolithium (0.01 mol of a solution in pentane) was added to a stirred, ice-cooled solution of benzyltrimethylsilane (1.64 g, 0.01 mol) in HMPA (10 mL). Stirring was continued for 2 hours, when a solution of benzaldehyde (1.1 g, 0.01 mol) in diethyl ether (5 mL) was added. The ice bath was removed and the reaction mixture stirred at ambient temperature for 1 hour. The mixture was poured into ice-cooled 1% hydrochloric acid (25 mL). The ethereal layer was separated, and the aqueous layer extracted with ether (2 × 10 mL). The combined extracts were washed with water, dried (Na₂SO₄–Na₂CO₃), and evaporated to give a brown liquid (2.4 g). Recrystallization of this crude material from ethanol gave *trans*-stilbene (0.6 g); mp 124–125°. The filtrate was evaporated to give *cis*-stilbene (0.3 g); bp 105–106°/5 mm Hg. Total yield of stilbene was 50%.

6.1.2.3. 1,1-Diphenyl-2-(2-pyridyl)-1-ethene (96)

A 15% solution of *n*-butyllithium (13 g, 0.03 mol) in hexane was added to a solution of diisopropylamine (0.03 mol) in tetrahydrofuran (54 mL) at –75°. To the solution, 2-(trimethylsilylmethyl)pyridine (0.03 mol) was added dropwise over 5 minutes. After an additional 10 minutes at this temperature, the mixture was treated with benzophenone (0.045 mol) in tetrahydrofuran. The resultant mixture was stirred for 1 hour at –75° and then allowed to warm to room temperature with stirring over 2 hours. The reaction mixture was quenched with water (60 mL) and extracted with diethyl ether. The extracts were dried, evaporated, and recrystallized from petroleum ether to give the alkene (53%); mp 120–121.5°; ¹H NMR (CCl₄) δ 6.5–7.55 (12H, m), 8.48 (1H, dd).

6.1.2.4. Reaction of 1-Triphenylsilyl-1-hexyllithium with Benzaldehyde (Alkylolithium Addition to a Vinylsilane) (91)

A solution of triphenylvinylsilane (1.43 g, 5 mmol) in diethyl ether (50 mL) was added dropwise over 1.75 hours to a stirred solution of *n*-butyllithium (2.2 mL,

5 mmol) in diethyl ether. After 5 minutes, benzaldehyde (0.53 g, 5 mmol) was added over 15 minutes to the stirred reaction mixture. The mixture was then stirred under reflux for 30 hours, cooled, and poured into 10% aqueous ammonium chloride solution (50 mL). The ether layer was separated and the aqueous phase was extracted with ether (2 × 25 mL). The combined extracts were dried (Na₂SO₄) and evaporated to give 2.2 g of a mixture of pale yellow oil and white solid. Treatment with *n*-pentane and filtration afforded triphenylsilanol (0.6 g); mp 156–157.5°. Evaporation of the filtrate gave an oil, which upon distillation yielded 1-phenylheptene (0.4 g, 46%) as a 1:1 mixture of the *E* and *Z* isomers (VPC analysis); bp 46°/0.01 mm Hg; IR (neat) 2910, 2830, 2770, 1610, 1502, 1478, 1458, 973, 772, 747, 704, 697, cm⁻¹; ¹H NMR (CCl₄) δ 0.9 (3H, t) 1.48 (6H, m), 2.2 (2H, m), 6.13 (2H, m), 7.23 (5H, br s).

6.1.2.5. 1-Phenylbut-1-ene (Reductive Cleavage of a Phenylthio Group with Lithium Naphthalenide) (157)

Phenyl(phenylthio)(trimethylsilyl)methane (2.72, 0.01 mol) in tetrahydrofuran (10 mL) was added to a solution of lithium naphthalenide [prepared from lithium (0.14 g, 0.02 mol) and naphthalene (2.56 g, 0.02 mol)] in tetrahydrofuran (50 mL) at -78°. The mixture was stirred for 30 minutes at this temperature. Pentanal (0.01 mol) in tetrahydrofuran (5 mL) was added and the mixture allowed to warm slowly to room temperature. Hydrochloric acid (2 M, 50 mL) was added and the mixture stirred overnight. The mixture was poured into saturated aqueous ammonium chloride solution (50 mL) and extracted with diethyl ether (3 × 50 mL). The extracts were washed with 2 M sodium hydroxide solution (2 × 40 mL) and saturated aqueous sodium chloride solution, dried (Na₂SO₄), and the alkene isolated by fractional distillation (1.24 g, 85%) as a 1:1 mixture of the *E* and *Z* isomers.

6.1.3. (4-*tert*-Butylcyclohexylidene)cyclohexylmethane [Displacement of a Phenylthio Group by Lithium 1-(Dimethylamino)naphthalenide] (155)

6.1.3.1.1. Lithium 1-(Dimethylamino)naphthalenide

To a flame-dried two-necked flask, which was continuously purged with argon and equipped with a glass-coated stirring bar, was added tetrahydrofuran (10 mL) and lithium ribbon (40 mg, 5.8 mmol). The mixture was cooled to -45 to -55° by a 1-hexanol/dry ice bath. 1-(Dimethylamino)naphthalene (0.84 mL, 0.87 g, 5.1 mmol) was added slowly. The dark green color of the radical anion appeared within 10 minutes and was complete after 3.5 hours of rapid stirring. This procedure yielded an approximately 0.5 M solution of lithium 1-(dimethylamino)-naphthalenide.

6.1.3.1.2. 1-(Phenylthio)-1-(trimethylsilyl)-4-*tert*-butylcyclohexanone

A solution of 1,1-bis(phenylthio)-4-*tert*-butylcyclohexanone (1.44 g, 4.05 mmol) in tetrahydrofuran (5 mL) was added to a solution of lithium 1-(dimethylamino)-naphthalenide (10.4 mmol) in tetrahydrofuran (20 mL) at -78° and the resultant mixture was stirred for 15 minutes. Freshly distilled

chlorotrimethylsilane (0.60 mL, 0.51 g, 4.7 mmol) was added, and within 1 minute the reaction was quenched with excess water at -78° . The solvent was removed under reduced pressure and the residue taken up in diethyl ether. This mixture was washed twice with 5% sodium hydroxide solution and twice with 5% sulfuric acid and saturated aqueous sodium hydrogen carbonate solution, dried (MgSO_4), and evaporated to give the crude α -thiosilane. Column chromatography afforded

1-(phenylthio)-1-(trimethylsilyl)-4-*tert*-butylcyclohexanone (1.08 g, 83%); mp $83.1\text{--}83.9^{\circ}$; IR (CCl_4) 3090, 2950, 1440, 1400, 1370, 1250, 1120, 1020 cm^{-1} ; $^1\text{H NMR}$ (CCl_4) δ 0.23 (9H, s), 0.80 (9H, s), 0.97–2.00 (9H, s).

6.1.3.1.3. (4-*tert*-Butylcyclohexylidene)cyclohexylmethane

A solution of 1-(phenylthio)-1-(trimethylsilyl)-4-*tert*-butylcyclohexanone (0.20 g, 0.64 mmol) in tetrahydrofuran (1 mL) was added to a solution of lithium 1-(dimethylamino)naphthalenide (1.5 mmol) in tetrahydrofuran (3 mL) and the resultant mixture stirred for 4 minutes at -78° . Cyclohexanecarboxaldehyde (0.10 mL, 0.09 g, 0.08 mmol) was added and the mixture stirred for 15 minutes. The reaction was worked up as described in the previous procedure to give, after flash chromatography, the β -hydroxysilane; IR (CCl_4) 3625, 2925, 1440, 1335, 1225 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 0.13 (9H, s), 0.83 (9H, s), 0.66–1.97 (21H, m), 3.13 (1H, br m).

The alcohol was dissolved in tetrahydrofuran (3 mL) and treated with hexane-washed potassium hydride in tetrahydrofuran at room temperature for 1.5 hours. The resultant mixture was poured into ice water overlaid with diethyl ether. The organic layer was separated, dried (MgSO_4), and evaporated to give, after column chromatography (SiO_2 ; hexanes), the alkene (0.12 g, 80% overall); IR (neat) 2950, 2850, 1485, 1395, 1250 cm^{-1} ; $^1\text{H NMR}$ (CCl_4) δ 0.87 (9H, s), 0.57–2.80 (20H, m), 4.75–4.97 (1H, br d).

6.1.3.2. 3,4-Dimethoxystyrene (Displacement of a Stannyl Group) (167)

To a flame-dried flask with a serum-stopped side arm under nitrogen was added a solution of (tri-*n*-butylstannyl)(trimethylsilyl)methane (2.263 g, 6.00 mmol) in tetrahydrofuran (8 mL). The flask and contents were cooled to 0° , when *n*-butyllithium (4.0 mL of a 1.5 M solution in hexane, 6.0 mmol) was added dropwise with stirring. After 30 minutes, the mixture was cooled to -78° and veratraldehyde (998 mg, 6.0 mmol) in tetrahydrofuran (2 mL) added dropwise. The reaction was stirred for 5 minutes at -78° , then quenched with water. The mixture was extracted with hexane (3×10 mL). The combined extracts were washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. Rapid filtration of this crude product through silica (15 g) with hexane afforded tetra-*n*-butyltin (2.083 g, 100%). Further elution of the mixture with ethyl acetate and hexane (1:1) gave the β -hydroxysilane, which was then stirred with a two-phase mixture comprised of hexane (10 mL) and 50% acetic acid (10 mL) for 30 minutes. The layers were then separated and

the organic phase washed with 5% aqueous sodium hydrogen carbonate solution and water, dried (Na_2SO_4), and concentrated under reduced pressure. Shortpath column chromatography eluting with hexane and ethyl acetate (9:1) gave 3,4-dimethoxystyrene (760 mg, 77%).

6.1.3.3. 1,2-Tridecadiene (172)

n-Butyllithium (0.024 mol) was added slowly to a solution of α -bromovinyltriphenylsilane (8.8 g, 0.024 mol) in diethyl ether (60 mL) at -24° and the resultant mixture stirred for 1.5 hours. Undecanal (0.024 mol) in diethyl ether (10 mL) was added slowly and the reaction mixture stirred at -24° for 1 hour. Stirring was continued overnight at ambient temperature. The mixture was then poured into 10% hydrochloric acid (50 mL). The organic phase was separated, washed with water (50 mL), dried (MgSO_4), and evaporated under reduced pressure to give the crude alcohol. This alcohol was dissolved in carbon tetrachloride (25 mL) and a 25% excess of thionyl chloride added. The reaction mixture was stirred for 2 hours and then evaporated to give the crude chloride. This crude chloride was dissolved in dimethyl sulfoxide (25 mL per gram of tetraethylammonium fluoride used) and a 10% excess of tetraethylammonium fluoride added. The mixture was stirred for 2 hours at room temperature. The mixture was partitioned between diethyl ether (25 mL) and water (25 mL). The ethereal phase was separated, dried (MgSO_4), and evaporated to give the crude allene. The crude product was treated with hexane (10 mL) and cooled. Filtration gave triphenylsilanol, while distillation afforded 1,2-tridecadiene (44%); bp $63\text{--}64^\circ/0.1$ mm Hg; IR 1960 cm^{-1} ; ^1H NMR δ 0.75–2.25 (21H, m), 4.6 (2H, m), 5.05 (1H, m).

6.1.4. α , β -Unsaturated Esters

6.1.4.1.1. Ethyl Trimethylsilylacetate (192)

In a 2-L three-necked flask equipped with a mechanical stirrer, dropping funnel, and condenser arranged for distillation were placed benzene (500 mL) and strips of freshly sandpapered zinc (31.7 g, 0.5 mol). To ensure dryness, 75 mL of the benzene was distilled off, and the condenser replaced by a reflux condenser with a calcium chloride guard tube. A solution of redistilled chlorotrimethylsilane (43.5 g, 0.40 mol) and ethyl bromoacetate (83.5 g, 0.50 mol) in benzene (100 mL) and anhydrous diethyl ether (100 mL) was added over 30 minutes to maintain a gentle reflux. A crystal of iodine can be used to initiate the reaction. Occasionally the reaction can be vigorous and require cooling. After the addition was complete, the mixture was heated under reflux until all of the zinc had dissolved, 1–3 hours. The mixture was cooled in an ice bath, and 1 M hydrochloric acid (400 mL) added over 15 minutes with stirring. The mixture was stirred for a further 5 minutes and separated. The organic layer was washed with 1 M hydrochloric acid, and the combined aqueous layers extracted with ether. The combined organic extracts were washed with water, saturated sodium hydrogen carbonate solution, water again, and dried. Frequently, a precipitate formed in the hydrogen carbonate

solution, but this was drawn off and discarded. The solvents were distilled. Fractional distillation gave impure ethyl trimethylsilylacetate (46.1 g, 72%); bp 76–77°/40 mm Hg; $^1\text{H NMR}$ (CH_2Cl_2) δ 0.15 (9H, s), 1.24 (3H, t), 1.87 (2H, s), 4.02 (2H, q).

6.1.4.1.2. *tert*-Butyl Trimethylsilylacetate (191, 455)

tert-Butyl acetate (32.95 mL, 28.4 g, 0.245 mol) in tetrahydrofuran (40 mL) was added dropwise to a solution of lithium diisopropylamide [from diisopropylamine (37.25 mL, 27.0 g, 0.267 mol) and *n*-butyllithium (150 mL of a 1.67-M solution in hexane, 0.250 mol)] in tetrahydrofuran (400 mL) at -78° over 0.5 hour. The mixture was stirred for 1 hour at this temperature and then chlorotrimethylsilane (26.1 g, 30.5 mL, 0.241 mol) was added. The reaction mixture was allowed to warm to room temperature overnight. The reaction was quenched by pouring into saturated aqueous ammonium chloride solution (50 mL). The mixture was extracted with diethyl ether (3×100 mL). The combined extracts were washed with saturated aqueous sodium chloride solution (75 mL), dried (Na_2SO_4), concentrated under reduced pressure, and distilled to give the α -silyl ester (29.7 g, 66%); bp $67^\circ/13$ mm Hg; IR (film) 1740 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 0.09 (9H, s), 0.88 (9H, s), 1.80 (2H, s).

6.1.4.1.3. Ethyl 2-Undecenoate (40)

Dicyclohexylamine (365 mg, 2.0 mmol) was dissolved in dry tetrahydrofuran (10 mL). The solution was cooled to -78° and then treated with *n*-butyllithium (1.35 mL of a 1.5 M solution in hexane). The mixture was stirred for 15 minutes. A solution of ethyl trimethylsilylacetate (320 mg, 2.0 mmol) in tetrahydrofuran (1.0 mL) was added dropwise at -78° , and the resultant solution was stirred at this temperature for 10 minutes when *n*-nonanal (142 mg, 1.0 mmol) in tetrahydrofuran (1 mL) was added dropwise. The mixture was stirred at -78° for 1 hour, at -25° for 1 hour, and at 25° for 1 hour. Finely ground sodium hydrogen sulfate monohydrate (0.22 g) was added and the mixture stirred for 10 minutes. The solid was filtered off and water added to the filtrate. This solution was extracted with ethyl acetate (3×5 mL). The combined extracts were dried, evaporated, and chromatographed on a silica thin-layer plate to give ethyl (*Z*)-2-undecenoate (51 mg, 24%); IR (neat) 1724, 1646, 1470, 1418, 1186, 1040, 822 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 0.68–1.04 (3H, m), 1.05–1.75 (12H, m), 1.24 (3H, t), 2.57 (2H, br d), 4.06 (2H, q), 5.62 (1H, d, $J = 9.3$ Hz), 6.05 (1H, dt, $J = 6.3$ and 9.3 Hz), and ethyl (*E*)-2-undecenoate (128 mg, 58%); IR (neat) 1724, 1656, 1470, 1270, 1185, 1047, 985 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) 0.70–1.08 (3H, m), 1.09–1.85 (12H, m), 1.28 (3H, t), 2.18 (2H, br t), 4.18 (2H, q), 5.74 (1H, d, $J = 15$ Hz), 6.86 (1H, dt, $J = 7$ and 15 Hz).

6.1.4.1.4. *tert*-Butyl Cyclohexylideneacetate (201)

Diisopropylamine (3.6 mL, 25 mmol) was added to *n*-butyllithium (12.5 mL of a 1.5 M solution in hexane) over 2 minutes at 0° . The hexane was removed under reduced pressure, and the residue dissolved in tetrahydrofuran (25 mL).

The solution was cooled to -78° , and *tert*-butyl trimethylsilylacetate (5.5 mL, 25 mmol) added dropwise over 2 minutes. The mixture was stirred for 10 minutes and then cyclohexanone (2.6 mL, 25 mmol) was added. The solution was allowed to come to room temperature before it was quenched by the addition of 3 M hydrochloric acid (25 mL). The product was isolated by extraction with pentane and vacuum distilled to give the ester (4.5 g, 90%); bp 121–123/16 mm Hg.

6.1.5. Cyclohexylidenepropionaldehyde (Use of an α -Silylimine) (232)

6.1.5.1.1. Silylation of Propionaldehyde *tert*-Butylimine

Propionaldehyde imine (7.23 mL, 63.8 mmol) was added to a stirred solution of lithium diisopropylamide (66.0 mmol) in tetrahydrofuran (100 mL) at 0° under argon. The solution was treated with chlorotrimethylsilane (8.12 mL, 64.0 mmol) with stirring and cooling. The reaction mixture was warmed to 0° over 3.5 hours, poured into water (150 mL), and extracted with diethyl ether. The organic extracts were washed with saturated sodium chloride solution, dried (K_2CO_3), concentrated, and distilled to give the α -silylimine (8.5 g, 73%); bp 175–178 $^{\circ}$.

6.1.5.1.2. Cyclohexylidenepropionaldehyde

The silylated propionaldehyde imine, prepared as described above (0.493 g, 2.50 mmol), was added to a solution of lithium diisopropylamide (2.60 mmol) in tetrahydrofuran (9 mL) at 0° under argon. The reaction mixture was stirred for 15 minutes, then cooled to -78° and treated with cyclohexanone (0.26 mL, 2.50 mmol). The resultant mixture was warmed to -20° over 2.5 hours, then quenched with water (3 mL). Solid oxalic acid was added to bring the pH to 4.5. The mixture was stirred for 30 minutes, then poured into saturated aqueous sodium chloride solution (10 mL), and extracted with diethyl ether. The extracts were washed with sodium hydrogen carbonate solution, dried (K_2CO_3), concentrated under reduced pressure, and distilled (short path) to give the enal (310 mg, 90%); bp 80–85 $^{\circ}$ (bath)/0.07 mm Hg; IR (CCl_4) 1675 cm^{-1} ; 1H NMR (CCl_4) δ 1.69 (CH_3 and CH_2 protons), 2.37 and 2.64 (γ - CH_2 protons) and 10.1 (CHO).

6.1.5.2. Cinnamionitrile (224)

Trimethylsilylacetone nitrile (0.567 g, 5.0 mmol) was added to a solution of lithium diisopropylamide [formed from diisopropylamine (0.516 g, 5.1 mmol) and *n*-butyllithium (4.6 mL of a 1.1 M solution)] in tetrahydrofuran (5 mL) at -78° . The mixture was stirred for 40 minutes at this temperature. A solution of benzaldehyde (0.529 g, 4.99 mmol) in tetrahydrofuran (5 mL) was added at -78° and the mixture stirred for 1 hour at this temperature and 4 hours at room temperature. The reaction was quenched with aqueous ammonium chloride solution and extracted with dichloromethane (6 \times 20 mL). The combined extracts were washed with saturated aqueous sodium chloride solution, dried ($MgSO_4$), and concentrated under reduced pressure to give the α , β

-unsaturated nitrile (0.499 g, 77%) as a 1:1 mixture of *E* and *Z* isomers after column chromatography.; IR (CCl₄) 2235, 1620 cm⁻¹; ¹H NMR (CCl₄) δ 5.42 (1H, d, *J* = 12 Hz), 5.86 (1H, d, *J* = 16.5 Hz), 7.10 (1H, d, *J* = 12 Hz), 7.37 (1H, d *J* = 16.5 Hz), 7.4–7.9 (5H, m).

6.1.5.3. 2,3-Dimethyl-1-phenylthiobut-1-ene (157)

n-Butyllithium (7.15 mL of a 1.4 M solution in hexane, 10 mmol) was added to a solution of phenylthiotrimethylsilylmethane (1.96 g, 10 mmol) in tetrahydrofuran (25 mL) at 0°. After 0.5 hour, the carbonyl compound (10 mmol) was added and the mixture allowed to come to room temperature overnight. The mixture was poured into saturated aqueous ammonium chloride solution (50 mL) and extracted with ether (3 × 25 mL). The combined extracts were washed with 2 M sodium hydroxide solution (30 mL) and saturated aqueous sodium chloride solution (30 mL), dried (Na₂SO₄), evaporated under reduced pressure and chromatographed to give the vinyl sulfide (1.31 g, 68%) as an oil; IR (CHCl₃) 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 1.0 (6H, 2 × d), 1.75 (3H, br s), 2.0–2.5 (1H, m), 5.75 and 5.90 (1H, 2s, ratio 1:1), 7.15 (5H, br s).

6.1.5.4. 4,4-Dimethylcyclohex-2-en-1-ylidenemethyl Phenyl Sulfone (253)

n-Butyllithium (1.0 equivalent of a hexane solution) was added to a stirred solution of phenyl trimethylsilylmethyl sulfone (1.0 eq) in 1,2-dimethoxyethane (5 mL mmol⁻¹ sulfone) under argon at –78°. The pale yellow solution was maintained at –78° for 20 minutes while the carbonyl compound (1.0 eq) was added by syringe, either neat or as a solution in 1,2-dimethoxyethane. The reaction mixture was allowed to warm to room temperature immediately, whereupon aqueous ammonium chloride solution was added. The layers were separated, dried, evaporated, and purified by chromatography to give the vinyl sulfone (81%) as a 1:1 mixture of the *E* and *Z* isomers; IR (CH₂Cl₂) 3044, 2958, 2867, 1619, 1574, 1303, 1145 cm⁻¹; ¹H NMR (CDCl₃) δ 1.03 (3H, s), 1.05 (3H, s), 1.50–1.62 (2H, m), 2.39 and 2.90 (2H, m), 5.85 (0.5H, d *J* = 10 Hz), 5.95–6.10 (2H, m), 7.21 (0.5H, dd, *J* = 10 and 1 Hz), 7.50–7.65 (3H, m), 7.90–7.95 (2H, m).

6.1.5.5. Diethyl 3-Methyl-1-butenylphosphonate (239)

n-Butyllithium (25 mmol of a 23% solution in hexane) was added to a solution of diethyl trimethylsilylmethylphosphonate (5.6 g, 25 mmol) in tetrahydrofuran (10 mL) and the mixture stirred for 1.5 hours. Isobutyraldehyde (25 mmol) was added and, after a further 2 hours at 25°, saturated aqueous sodium chloride solution (25 mL). The layers were separated and the aqueous phase was extracted with diethyl ether, dried (MgSO₄), and concentrated to give the vinyl phosphonate (92%) as a 1:2.4 mixture of the *E* and *Z* isomers, which were separated by preparative GLPC on a 10-ft 20% Carbowax 20 M-on-firebrick column at 150°. The major isomer eluted first; ¹H NMR (CDCl₃) δ 1.10 (6H, d), 1.4 (6H, t), 3.32 (1H, m), 4.10 (4H, q), 5.4 (1H, dd, *J* = 12 and 20 Hz), 6.2 (1H, ddd, *J* = 12, 10, and 52 Hz), followed by the *E* isomer; ¹H NMR 1.10 (6H, d),

1.36 (6H, t), 4.10 (4H, q), 5.58 (1H, t, $J = 18$ and 18 Hz), 6.8 (1H, ddd, $J = 18$, 7 , and 23 Hz).

6.1.5.6. 2-[Methoxy(trimethylsilyl)methyl]-2-adamantanol [Reaction of (Trimethylsilyl)methoxymethylithium] (277)

(Methoxymethyl)trimethylsilane (0.66 mL, 4.23 mmol) in tetrahydrofuran (6.0 mL) was cooled to -78° and *sec*-butyllithium (3.0 mL of a 1.4 M solution in cyclohexane, 4.23 mmol) slowly added by syringe. The mixture was warmed to -25° and then held at this temperature for 0.5 hour. The pale yellow solution was cooled to -35° and adamantanone (0.57 g, 3.8 mmol) added. The mixture was allowed to slowly warm to room temperature over 1.5 hours, when it was quenched with saturated aqueous ammonium chloride solution (30 mL) and extracted with diethyl ether (2×30 mL). The ethereal layer was washed with water (2×20 mL) and saturated aqueous sodium chloride solution (10 mL), dried (MgSO_4), and evaporated under reduced pressure to give the alcohol (0.91 g, 89%); mp 65 – 67° (petroleum ether/ethyl acetate); IR (nujol) 3500, 2900, 2850, 1450, 1375, 1320, 1250, 1170, 1050, 990, 930, 910, 870, 840 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 0.1 (9H, s), 1.65 (10H, br s), 1.7 (4H, br s), 2.2 (1H, br s), 3.4 (3H, s).

6.1.5.7. 2-(3-Phenyl-2-propenylidene)-1,3-dithiane (305)

n-Butyllithium (11.25 mL of a 2.2 M solution in hexane, 25 mmol) was added to a solution of 2-trimethylsilyl-1,3-dithiane (4.80 g, 25 mmol) in tetrahydrofuran (25 mL) and the resultant mixture stirred for 15 minutes at 0° . Cinnamaldehyde (25 mmol) was added and the temperature maintained at 0° for 15 minutes and 25° for 15 minutes. The reaction was quenched with saturated sodium chloride solution (37.5 mL) and extracted with diethyl ether (2×25 mL). The extracts were dried (MgSO_4) and evaporated to give the crude product, which separated as yellow crystals from hexane–ether; mp 84° ; $^1\text{H NMR}$ (CDCl_3) δ 2.0–2.4 (2H, m), 2.8–3.1 (4H, m), 6.58 (1H, d, $J = 15$ Hz), 6.63 (1H, d, $J = 10$ Hz), 7.0–7.6 (6H, m).

6.1.5.8. *tert*-Butyl 2-(Tri-*n*-butylstannyl)-2-hexenoate (287)

A 25-mL, flame-dried flask fitted with a serum-stoppered side arm was cooled in an ice-water bath. *n*-Butyllithium (2.2 mmol of a solution in hexane) was placed in the flask and diisopropylamine (0.35 mL, 2.5 mmol) was added dropwise. When the addition was complete, the solvent was removed under reduced pressure. The residue was dissolved in tetrahydrofuran (2.5 mL) and HMPA (0.70 mL, 4.0 mmol) was added. The flask was cooled with a dry ice–acetone bath and a solution of *tert*-butyl α -(tri-*n*-butylstannyl)- α -(trimethylsilyl)acetate (0.9573 g, 2.0 mmol) in tetrahydrofuran (1.0 mL) was added dropwise. The reaction was stirred for 10 minutes at -78° , and then at -23° for 30 minutes. The solution was cooled to -78° , and butyraldehyde (0.18 mL, 2.0 mmol) was added. The mixture was stirred for a further 10 minutes, then hydrolyzed with saturated aqueous ammonium chloride solution

and extracted with petroleum ether. The product, *tert*-butyl-2-(tri-*n*-butylstannyl)-2-hexenoate, was purified by TLC on silica eluting with petroleum ether–dichloromethane (1:1) and was obtained as a 46:54 mixture of the *E* and *Z* isomers (0.4794 g, 51%); IR (neat) 1690 cm⁻¹; ¹H NMR (CDCl₃) δ 0.7–1.7 (32H, m), 1.5 (9H, s), 2.3 (2H, m) 5.96 and 7.3 (1H, t).

6.1.6. *N*-6-Methyl-2,4-di-*tert*-butylsulfinylanilide (227)

6.1.6.1.1. *N*-Trimethylsilyl-6-methyl-2,4-di-*tert*-butylaniline

n-Butyllithium (20.6 mL of a 1.6 M solution in hexane, 33 mmol) was added gradually to a solution of 6-methyl-2,4-di-*tert*-butylaniline (30 mmol) in tetrahydrofuran (60 mL) at –78°. The mixture was stirred for 1 hour at room temperature, then chlorotrimethylsilane (4.6 mL, 36 mmol) was added at –78°. The reaction mixture was stirred at room temperature for 15 minutes, the solvent was evaporated, and the residue distilled to give the *N*-silylamine (78%); bp 85°/0.2 mm Hg; IR (neat) 3440, 1255, 836 cm⁻¹; ¹H NMR (CDCl₃) δ 0.21 (9H, s), 1.41 (9H, s), 2.27 (3H, s), 2.90 (1H, s), 6.95 (1H, d), 7.15 (1H, d).

6.1.6.1.2. *N*-6-Methyl-2,4-di-*tert*-butylsulfinylanilide

A solution of *n*-butyllithium (13.75 mL of a 1.6 M solution in hexane, 22 mmol) was added to a stirred solution of the *N*-silylamine (20 mmol, prepared as described above) in tetrahydrofuran (50 mL) at 0°. The solution was stirred for 1 hour at room temperature and added to excess sulfur dioxide in tetrahydrofuran (50 mL) at –78°. This mixture was stirred for 1 hour at room temperature. The reaction was quenched by the addition of saturated aqueous ammonium chloride solution (20 mL). The organic layer was separated, dried (MgSO₄), evaporated, and the residue recrystallized from methanol to give the *N*-sulfinylamine (80%); mp 53–55°; IR (KBr) 1271, 1181 cm⁻¹.

6.1.7. Phenylacetaldehyde [Reaction of Chloro(trimethylsilyl)methylithium, Formation of an α, β -Epoxy silane and Its Opening] (269)

6.1.7.1.1. (*E,Z*)-3-Phenyl-2-trimethylsilyloxirane

sec-Butyllithium as a solution in cyclohexane (1.1-*M*, 1.05 eq.) was added to a stirred solution of chloromethyl(trimethylsilyl)methane (6.15 mmol) in tetrahydrofuran (8 mL) at –78° under argon. After 5 minutes, *N,N,N*φ,*N*φ-tetramethylethylenediamine (1.05 eq.) was added and the mixture stirred for 0.5 hour while allowing the temperature to rise to –55°. Benzaldehyde (0.53 g, 4.93 mmol) was added to the pale yellow solution at –55°. The solution was maintained at –50° for 0.5 hour, then warmed to 20° over 3 hours. The mixture was poured into 0.5 M hydrochloric acid (25 mL), extracted with dichloromethane (3 × 30 mL), dried (MgSO₄), and evaporated to give the epoxide as an oil (0.87 g, 95–98% pure, 3.4:1 ratio of *Z*:*E* isomers by GLC); IR (neat) 1605, 1595, 1248, 842, 750 cm⁻¹; ¹H NMR (CCl₄) δ 0.19 (9H, s), 0.31 (9H, s), 2.48 (1H, d), 2.68 (1H, d), 3.86 (1H, d), 4.40 (1H, d), 7.47 (5H, s).

6.1.7.1.2. Hydrolysis to Phenylacetaldehyde Dimethylacetal

The α , β -epoxysilane (0.20 g, prepared as described above) was stirred with 10% aqueous methanol (5 mL) and boron trifluoride etherate (0.095 mL) at -5° . The mixture was warmed to 20° . After 2 hours, the reaction mixture was poured into 0.5 M hydrochloric acid (20 mL). The mixture was extracted with dichloromethane (3×20 mL), dried (MgSO_4), and evaporated to give the acetal (0.14 g, 82%), identical with an authentic sample.

6.1.7.1.3. Hydrolysis to Phenylacetaldehyde

The α , β -epoxysilane (0.19 g, prepared as described above) was stirred with 20% aqueous tetrahydrofuran (2 mL), and 70% perchloric acid (0.01 mL) was added. After 4 hours, the mixture was poured into water (20 mL), extracted with dichloromethane (3×20 mL), dried (MgSO_4), and evaporated under reduced pressure at 30° to give the aldehyde (0.14 g, 85%); 2,4-dinitrophenylhydrazone: mp $230-235^\circ$.

7. Tabular Survey

The following tables contain examples of the Peterson olefination reaction as defined in the introduction to this chapter. The tables also include the eliminations of β -hydroxysilanes, although the origin of some of these compounds may not have been by a Peterson protocol. A table has been compiled for noncarbonyl-derived electrophiles. Related reactions, such as the homo-Peterson reaction, are not contained in the tabular survey. The literature survey includes articles appearing up to December 1986.

The tables are arranged by substituent in the α -silyl carbanion and appear in the same order as described in the text. Within each table, substances are arranged in order of increasing number of carbon atoms in the α -silyl carbanion, or β -hydroxysilane when applicable, and then by the heteroatom substituent. Only the carbon atoms contained within the carbon chain directly bonded to the silicon atoms are included in the count. With silanes similar in every other regard, the size of the silyl substituent is used to determine the order of appearance. The electrophiles are ordered in a similar manner to the α -silyl carbanions.

The titles of the tables are self-explanatory. All reactions which give rise to conjugated or homo-conjugated carbon-carbon unsaturation are contained in Tables IV–XI. Products that contain conjugation with heteroatom-derived functional groups are contained in the appropriate heteroatom table.

In tables which imply stereochemistry, such as Table III, entries between two columns separated by a comma denote that the stereochemistry is not cited in the literature or a mixture of isomers is used. Isomer ratios of the alkene products are quoted only when noted in the original citation.

In Tables I and II the formation of trimethylsilylmethyl lithium is inferred from the chloride, unless specifically stated, as this compound is commercially available.

The reagent column indicates the reagent necessary for the generation of the α -silyl carbanion and/or elimination from the β -hydroxysilane. Aqueous workup is not included. The product column indicates all products with yields in parentheses; a dash denotes that no specific yield is given.

Abbreviations for some reagents are used in the tabular material. Short forms of some groups are also used when that group is not directly involved in the reaction.

Ac acetyl

BF ₃ ·OEt ₂	boron trifluoride etherate
diglyme	diethylene glycol dimethyl ether
DME	1,2-dimethoxyethane
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
Et ₂ O	diethyl ether
HMPA	hexamethylphosphoric triamide
KDA	potassium diisopropylamide
LDA	lithium diisopropylamide
LDMAN	lithium 1-(dimethylamino)naphthalenide
LiC ₁₀ H ₈	lithium naphthalenide
LiTMP	lithium 2,2,6,6-tetramethylpiperidide
MCPBA	<i>m</i> -chloroperoxybenzoic acid
Mes	mesityl
MgBr ₂ ·OEt ₂	magnesium bromide etherate
py	pyridine
rt	room temperature
THF	tetrahydrofuran
Thp	tetrahydropyranyl
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TsOH	<i>p</i> -toluenesulfonic acid

Table I. Preparation of Hydrocarbon Alkenes

[View PDF](#)

Table II. Formation of β -Hydroxysilanes

[View PDF](#)

Table III. Eliminations of β -Hydroxysilanes

[View PDF](#)

Table IV. Reactions of Silanes Containing Unsaturation without Isolation of a β -Hydroxysilane

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Table V. Preparation of Unsaturated β -Hydroxysilanes

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Table VI. Eliminations from Unsaturated β -Hydroxysilanes

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Table VII. Formation of α , β -Unsaturated Carboxylic Acid Derivatives

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Table VIII. Formation of α , β -Unsaturated Carbonyl Compounds

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Table IX. Nitrogen-Containing α -Silyl Carbanions

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Table X. Sulfur-Containing α -Silyl Carbanions

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Table XI. Selenium-Containing α -Silyl Carbanions

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Table XII. Preparation of Vinyl Selenides

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Table XIII. Formation of Vinylsilanes

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Table XIV. Phosphorus-Containing α -Silyl Carbanions

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Table XV. Reactions of Oxygen-Containing α -Silyl Carbanions

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Table XVI. Elimination of β -Hydroxysilanes to Give Vinyl Ethers

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Table XVII. Other Miscellaneous α -Silyl Carbanions Containing a Heteroatom Substituent

[View PDF](#)

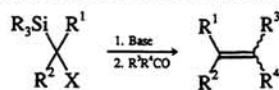
Table XVIII. Formation of Alkenes with Two Heteroatom Substituents

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Table XIX. Related Reactions with Other Electrophiles

[View PDF](#)

TABLE I. PREPARATION OF HYDROCARBON ALKENES




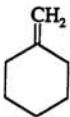
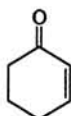
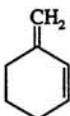
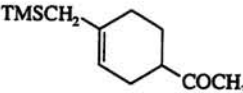
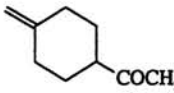
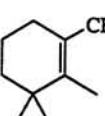
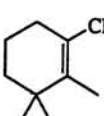
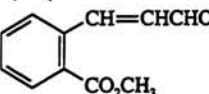
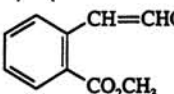
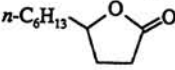
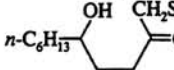
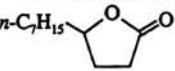
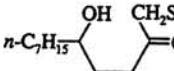


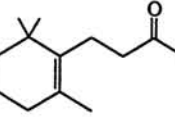
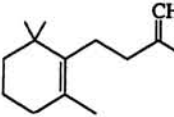
Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	R	R ¹	R ²				
C ₁							
Cl	CH ₃	H	H	(CH ₃) ₃ SiCH=CHCHO	1. Mg, Et ₂ O 2. TsOH, Et ₂ O	(CH ₃) ₃ SiCH=CHCH=CH ₂ (59)	103
					1. Mg, Et ₂ O 2. H ₂ O 3. NaH, THF, heat	 (>50)	92
				"	1. Mg, Et ₂ O 2. AcCl	" (100) ^a	91
					1. Li, Et ₂ O 2. AcCl	 (20)	91
				C ₆ H ₅ CO ₂ C ₂ H ₅	1. Mg, Et ₂ O ^b 2. SiO ₂	C ₆ H ₅ C(=CH ₂)CH ₂ Si(CH ₃) ₃ (49)	100
				"	1. Mg, Et ₂ O 2. H ₂ O	" (>50)	92
				"	3. NaH, THF, heat 1. Mg, Et ₂ O 2. SOCl ₂	" (57)	91
				CH ₃ CO(CH ₂) ₂ - CH=C(CH ₃) ₂	1. Li, Et ₂ O 2. SOCl ₂	CH ₂ =C(CH ₃)(CH ₂) ₂ CH=C(CH ₃) ₂ (53)	91
				C ₆ H ₅ (CH ₂) ₂ CO ₂ C ₂ H ₅	1. Mg, Et ₂ O ^b 2. SiO ₂	C ₆ H ₅ (CH ₂) ₂ C(=CH ₂)CH ₂ Si(CH ₃) ₃ (45)	100
					1. Mg, Et ₂ O 2. 35°, 2 h 3. HCl, CH ₃ OH	 (78)	106
				"	1. Mg, Et ₂ O 2. CsF, DMSO	" (46)	106
					1. Mg, Et ₂ O 2. TsOH, THF	 (90)	121
					1. Mg, Et ₂ O 2. AcOH, H ₂ O, C ₃ H ₁₂	 (75)	104
					1. Mg, Et ₂ O, heat 2. SiO ₂	 (45)	124
				HC≡C(CH ₂) ₂ - C≡C(CH ₂)CHO	1. Mg, Et ₂ O 2. AcCl, AcOH	CH ₂ =CH(CH ₂) ₂ C≡C(CH ₂) ₂ C≡CH (60)	140
				HC≡C(CH ₂) ₃ - C≡C(CH ₂) ₂ CHO	"	CH ₂ =CH(CH ₂) ₂ C≡C(CH ₂) ₃ C≡CH (60)	140
					1. Mg, Et ₂ O, heat 2. SiO ₂ , CHCl ₃	 (41)	124
					1. Mg, THF 2. SOCl ₂	 (60)	107
					1. Mg, Et ₂ O 2. AcCl	 (52)	91

TABLE I. PREPARATION OF HYDROCARBON ALKENES (Continued)

Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	R	R ¹	R ²				
					1. Mg, Et ₂ O, heat, 3 h 2. HCl, CH ₃ OH	(75)	106
					"	(73)	106
					"	(84)	105, 106
					1. Mg, Et ₂ O, heat, 11 h 2. HCl, CH ₃ OH	(42)	106
					"	(38)	106
					"	(25)	
					1. Mg, Et ₂ O 2. KH, THF	(62)	110
SC ₆ H ₅	CH ₃	H	H	<i>n</i> -C ₃ H ₇ CHO	1. LiC ₁₀ H ₈ , THF, -78° 2. HCl, H ₂ O "	CH ₂ =CHC ₃ H ₇ - <i>n</i> <i>E</i> : <i>Z</i> ~ 1:1 CH ₂ (69)	(64) 154, 157 157
					"	CH ₂ =CHC ₆ H ₅ (77)	154, 157
				C ₆ H ₅ CHO C ₆ H ₅ COCH ₃	"	CH ₂ =C(CH ₃)C ₆ H ₅ <i>E</i> : <i>Z</i> ~ 1:1	(83) 154, 157
				(C ₆ H ₅) ₂ CO	"	CH ₂ =C(C ₆ H ₅) ₂ (7)	154, 157
Si(CH ₃) ₃	CH ₃	H	H	<i>t</i> -C ₄ H ₉ COCH ₃ (C ₆ H ₅) ₂ CO	NaOCH ₃ , HMPA "	<i>t</i> -C ₄ H ₉ C(=CH ₂)C ₆ H ₅ (-) CH ₂ =C(C ₆ H ₅) ₂ (53)	166 166

TABLE I. PREPARATION OF HYDROCARBON ALKENES (Continued)

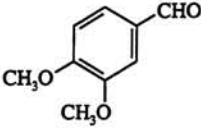
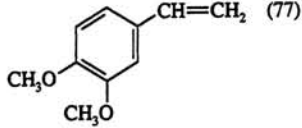
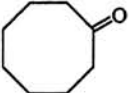
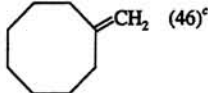
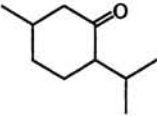
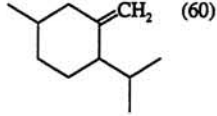
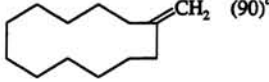
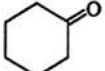
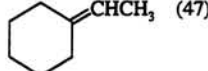
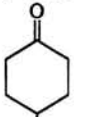
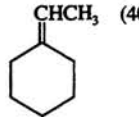

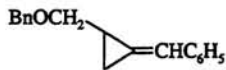
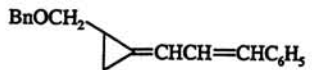
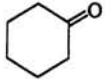
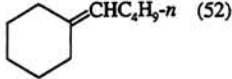
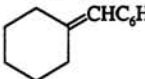
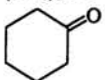
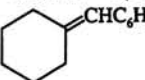
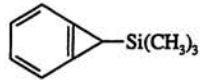
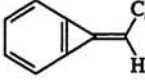
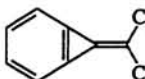
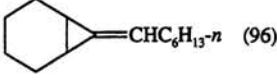
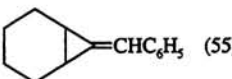
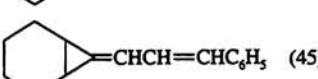
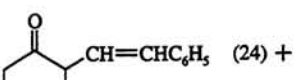
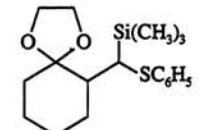
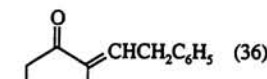
	Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	X	R	R ¹	R ²				
	Sn(C ₄ H ₉ -n) ₃	CH ₃	H	H	<i>p</i> -ClC ₆ H ₄ CHO	1. <i>n</i> -C ₄ H ₉ Li, THF, C ₆ H ₁₂ 2. AcOH, H ₂ O	CH ₂ =CHC ₆ H ₄ Cl- <i>p</i> (72)	167
						"	 (77)	167
						"	 (46) ^f	167
					<i>n</i> -C ₇ H ₁₅ CHO	1. <i>n</i> -C ₄ H ₉ Li, THF, C ₆ H ₁₂ 2. H ₂ SO ₄ , THF	CH ₂ =CHC ₇ H ₁₅ - <i>n</i> (61)	167
						1. <i>n</i> -C ₄ H ₉ Li, THF, C ₆ H ₁₂ 2. AcOH, H ₂ O	 (60)	167
					Cyclododecanone	"	 (90) ^f	167
					(C ₆ H ₅) ₂ CO	"	CH ₂ =C(C ₆ H ₅) ₂ (78)	167
C ₃	SC ₆ H ₅	CH ₃	CH ₃	H	(CH ₃) ₂ CO	1. LiC ₁₀ H ₈ , THF, -78° 2. HCl, H ₂ O	CH ₃ CH=C(CH ₃) ₂ (51)	157
					<i>n</i> -C ₃ H ₇ CHO	"	CH ₃ CH=CHC ₃ H ₇ - <i>n</i> (74)	154, 157
						"	 (47)	154, 157
					C ₆ H ₅ CHO	"	CH ₃ CH=CHC ₆ H ₅ (75)	154, 157
					C ₆ H ₅ COCH ₃	"	CH ₃ CH=C(CH ₃)C ₆ H ₅ (79)	154, 157
					(C ₆ H ₅) ₂ CO	"	CH ₃ CH=C(C ₆ H ₅) ₂ (80)	154, 157
	SeCH ₃	C ₂ H ₅	CH ₃	H		1. <i>n</i> -C ₄ H ₉ Li, THF 2. Acid or base ^d	 (40)	165
					C ₄ H ₉ - <i>t</i>	"		
					<i>n</i> -C ₁₀ H ₂₁ CHO	"	CH ₃ CH=CHC ₁₀ H ₂₁ - <i>n</i> (45)	165
					C ₆ H ₅ CH ₂ COC ₆ H ₅	"	CH ₃ CH=C(C ₆ H ₅)CH ₂ C ₆ H ₅ (90)	165
					C ₆ H ₅ CHO	1. LiC ₁₀ H ₈ , THF, -78° 2. HCl, H ₂ O	(CH ₃) ₂ C=CHC ₆ H ₅ (47)	157
					C ₆ H ₅ CHO	1. <i>n</i> -C ₄ H ₉ Li, THF, -95° 2. KH, THF	 (56)	238
					C ₆ H ₅ CH=CHCHO	"	 (46)	238
C ₅	SC ₆ H ₅	CH ₃	<i>n</i> -C ₄ H ₉	H	H ₂ CO	1. LiC ₁₀ H ₈ , THF, -78° 2. HCl, H ₂ O	<i>n</i> -C ₄ H ₉ CH=CH ₂ (58)	157

TABLE I. PREPARATION OF HYDROCARBON ALKENES (Continued)

	Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	X	R	R ¹	R ²				
					CH ₃ CHO	"	<i>n</i> -C ₄ H ₉ CH=CHCH ₃ (82)	154, 157
					(CH ₃) ₂ CO	"	<i>n</i> -C ₄ H ₉ CH=C(CH ₃) ₂ (61)	154, 157
					<i>n</i> -C ₅ H ₇ CHO	"	<i>n</i> -C ₄ H ₉ CH=CHC ₅ H ₇ - <i>n</i> (78)	154, 157
						"	 (52)	157
					C ₆ H ₅ CHO	"	<i>n</i> -C ₄ H ₉ CH=CHC ₆ H ₅ (86)	154, 157
					C ₆ H ₅ COCH ₃	"	<i>n</i> -C ₄ H ₉ CH=C(CH ₃)C ₆ H ₅ (76)	154, 157
					(C ₆ H ₅) ₂ CO	"	<i>n</i> -C ₄ H ₉ CH=C(C ₆ H ₅) ₂ (74)	154, 157
106	SC ₆ H ₅	CH ₃	<i>t</i> -C ₄ H ₉	H	(CH ₃) ₂ CO	"	<i>t</i> -C ₄ H ₉ CH=C(CH ₃) ₂ (<20) ^r	157
					C ₆ H ₅ CHO	"	<i>t</i> -C ₄ H ₉ CH=CHC ₆ H ₅ (32)	157
	C ₆	Li	C ₆ H ₅	<i>n</i> -C ₅ H ₁₁	H	C ₆ H ₅ CHO	<i>n</i> -C ₅ H ₁₁ CH=CHC ₆ H ₅ (50)	91, 92
						<i>n</i> -C ₅ H ₁₁ Li, Et ₂ O, CH ₂ =CHSi(C ₆ H ₅) ₃	<i>E:Z</i> = 1:1	
					(CH ₃) ₂ C=CH-(CH ₂) ₂ COCH ₃	"	<i>n</i> -C ₅ H ₁₁ CH=C(CH ₃)(CH ₂) ₂ -CH=C(CH ₃) ₂ (34)	91, 92
						<i>E:Z</i> = 1:1		
	SC ₆ H ₅	CH ₃	-(CH ₂) ₅ -		C ₆ H ₅ CHO	1. LiC ₁₀ H ₈ , THF, -78° 2. HCl, H ₂ O	 (38)	157
	C ₇	H	CH ₃	C ₆ H ₅	H	(CH ₃) ₂ CO	C ₆ H ₅ CH=C(CH ₃) ₂ (50)	3
						<i>n</i> -C ₄ H ₉ Li, TMEDA	 (52)	3
					C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CHC ₆ H ₅ (72)	3
					"	<i>n</i> -C ₄ H ₉ Li, HMPA	<i>E:Z</i> = 1:1 (50)	91, 92
					C ₆ H ₅ COCH ₃	"	<i>E:Z</i> = 2:1	
					(C ₆ H ₅) ₂ CO	<i>n</i> -C ₄ H ₉ Li, TMEDA	C ₆ H ₅ CH=C(CH ₃)C ₆ H ₅ (-) ^r	91, 92
					C ₆ H ₅ COCH ₃	<i>n</i> -C ₄ H ₉ Li, THF	C ₆ H ₅ CH=C(C ₆ H ₅) ₂ (77)	3
						"	 (10) ^r	97
					(C ₆ H ₅) ₂ CO	"	 (41) ^r	97
	Li	CH ₃	<i>i</i> -C ₃ H ₇ (CH ₂) ₃	H	<i>n</i> -C ₁₀ H ₂₁ CHO	<i>i</i> -C ₃ H ₇ (CH ₂) ₃ Li, Et ₂ O, CH ₂ =CHSi(C ₆ H ₅) ₃	<i>i</i> -C ₃ H ₇ (CH ₂) ₃ CH=CHC ₁₀ H ₂₁ - <i>n</i> (69)	91
					<i>n</i> -C ₆ H ₁₃ CHO	1. <i>n</i> -C ₄ H ₉ Li, THF, -95° 2. KH, THF	 (96)	238
					C ₆ H ₅ CHO	1. <i>n</i> -C ₄ H ₉ Li, THF, -95° 2. KOC ₄ H ₉ - <i>t</i> , THF	 (55)	238
					C ₆ H ₅ CH=CHCHO	"	 (45)	238
					C ₆ H ₅ CHO	1. LiC ₁₀ H ₈ , THF, -78° 2. HCl, H ₂ O	 (24) +	156
						"	 (36)	

106

C₆C₇

107

TABLE I. PREPARATION OF HYDROCARBON ALKENES (Continued)

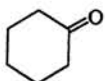
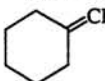
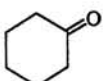
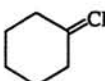
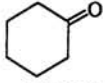
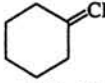
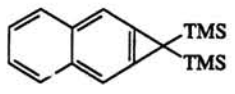
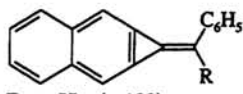
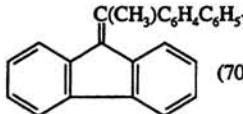
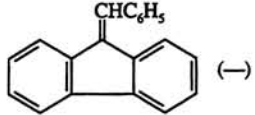
	Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	X	R	R ¹	R ²				
808	SC ₆ H ₅	CH ₃	C ₆ H ₅	H	H ₂ CO	"	C ₆ H ₅ CH=CH ₂ (62)	157
					CH ₃ CHO	"	C ₆ H ₅ CH=CHCH ₃ (71)	154, 157
					(CH ₃) ₂ CO	"	E:Z ~ 1:1	
					<i>n</i> -C ₃ H ₇ CHO	"	C ₆ H ₅ CH=C(CH ₃) ₂ (70)	154, 157
						"	C ₆ H ₅ CH=CHC ₃ H _{7-n} (85)	154, 157
						"	E:Z = 1:1	
						"	 (41)	157
C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CHC ₆ H ₅ (76)	154, 157					
	"	E:Z ~ 1:1						
	"	C ₆ H ₅ CH=C(CH ₃)C ₆ H ₅ (69)	154, 157					
	"	E:Z ~ 1:1						
SeCH ₃	CH ₃	<i>n</i> -C ₆ H ₁₃	H	(C ₆ H ₅) ₂ CO	1. <i>n</i> -C ₆ H ₅ Li, THF, 0° 2. Acid or base ^d	C ₆ H ₅ CH=C(C ₆ H ₅) ₂ (59)	154, 157	
				(C ₂ H ₅) ₂ CO		<i>n</i> -C ₆ H ₁₃ CH=C(C ₂ H ₅) ₂ (40)	165	
						 (40)	165	
SeCH ₃	C ₂ H ₅	<i>n</i> -C ₆ H ₁₃	H	<i>n</i> -C ₆ H ₁₃ CHO	"	<i>n</i> -C ₆ H ₁₃ CH=CHC ₆ H _{13-n} (90)	165	
					"	 (90)	165	
Si(CH ₃) ₃	CH ₃	C ₆ H ₅	H	<i>n</i> -C ₆ H ₁₃ CHO	NaOCH ₃ , HMPA	<i>n</i> -C ₆ H ₁₃ CH=CHC ₆ H _{13-n} (90)	165	
				<i>t</i> -C ₄ H ₉ CHO		C ₆ H ₅ CH=CHC ₄ H _{9-t} (26)	166	
						E:Z = 1:5.7		
				C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CHC ₆ H ₅ (79)	166	
				"	"	" (99)	37, 38	
				"	LiOC ₄ H _{9-t} , HMPA	E:Z = 1.32:1	(100)	
				"	KOC ₄ H _{9-t} , HMPA	E:Z = 1.43:1	(100)	
				"	KOC ₄ H _{9-t} , MgI ₂ , HMPA	E:Z = 1.30:1	(56)	
				"	NaOSi(CH ₃) ₃ , MgI ₂ , HMPA	E:Z = 1.85:1	(50)	
				"	"	E:Z = 1.83:1		
C ₈	Li	C ₆ H ₅	C ₆ H ₅ CH ₂	H	C ₆ H ₅ CHO	C ₆ H ₅ CH ₂ Li, Et ₂ O, CH ₂ =CHSi(C ₆ H ₅) ₃	C ₆ H ₅ CH ₂ CH=CHC ₆ H ₅ (40)	91
						<i>i</i> -C ₃ H ₇ (CH ₂) ₃ Li, Et ₂ O, CH ₂ =CHSi(C ₆ H ₅) ₃	<i>i</i> -C ₃ H ₇ (CH ₂) ₄ CH=CHC ₁₀ H _{21-n} (50)	91
						"	E:Z = 1:1	
SC ₆ H ₅	CH ₃	C ₆ H ₅	CH ₃	C ₆ H ₅ CHO	1. LiC ₁₀ H ₈ , THF, -78° 2. HCl, H ₂ O	C ₆ H ₅ C(CH ₃)=CHC ₆ H ₅ (<20) ^a	157	
C ₁₁					KOC ₄ H _{9-t} , THF	 (R)	97	
							R = H (~100)	
					"	R = CH ₃ (41)	97	
C ₁₃	H	CH ₃	9-Fluorenyl	<i>p</i> -C ₆ H ₄ COCH ₃	<i>n</i> -C ₄ H ₉ Li, THF, TMEDA, 0°	 (70)	94	

TABLE I. PREPARATION OF HYDROCARBON ALKENES (Continued)

X	Silane		R ²	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	R	R ¹					
Br	(C ₄ H ₉ -t) ₂	9-Fluorenyl	C ₆ H ₅ CHO	t-C ₄ H ₉ Li, C ₅ H ₁₂	 (—)	95	

^a The yield was determined by NMR.

^b At least two equivalents of the Grignard reagent are used.

^c The yield is based on recovered starting material.

^d No specific conditions are given.

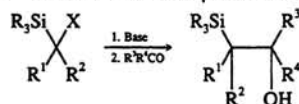
^e The yield was determined by GLC.

^f The product is obtained as a mixture of isomers.

^g The yield is overall from the parent hydrocarbon, which is silylated in situ.

^h The yield as determined by GLC and NMR.

TABLE II. FORMATION OF β -HYDROXYSILANES



	Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	X	R	R ¹	R ²				
C ₁	Br	CH ₃	H	H	(CH ₃) ₂ CO (E)-CH ₃ CH=CHCHO C ₆ H ₅ CHO (E)-C ₆ H ₅ CH=CHCHO C ₆ H ₅ CHO	Mg, Et ₂ O Mg, Et ₂ O, Cu ₂ Br ₂ Mg, Et ₂ O Mg, Et ₂ O, Cu ₂ Br ₂ <i>n</i> -C ₄ H ₉ Li, Et ₂ O	(CH ₃) ₃ SiCH ₂ COH(CH ₃) ₂ (52) (E)-(CH ₃) ₃ SiCH ₂ CHOHCH=CHCH ₃ (72) (CH ₃) ₃ SiCH ₂ CHOHC ₆ H ₅ (14) (E)-(CH ₃) ₃ SiCH ₂ CHOHCH=CHC ₆ H ₅ (90) (C ₆ H ₅) ₃ SiCH ₂ CHOHC ₆ H ₅ (81)	102 120 102 120 93
	Br	C ₆ H ₅	H	H	C ₆ H ₅ CHO	<i>n</i> -C ₄ H ₉ Li, Et ₂ O	(C ₆ H ₅) ₃ SiCH ₂ CHOHC ₆ H ₅ (81)	93
	Cl	CH ₃	H	H	HCO ₂ C ₂ H ₅ CH ₃ CHO (CH ₃) ₂ CO CH ₂ =CHCHO "	Mg, Et ₂ O " " " 1. Mg, Et ₂ O 2. H ₂ O 3. HRh[P(C ₆ H ₅) ₃] ₄	[(CH ₃) ₃ SiCH ₂] ₂ CHOH (50) (CH ₃) ₃ SiCH ₂ CHOHCH ₃ (—) (CH ₃) ₃ SiCH ₂ COH(CH ₃) ₂ (—) (CH ₃) ₃ SiCHOHCH=CH ₂ (65) (CH ₃) ₃ SiCOCH=CH ₂ (56)	100 2 3 118 61
					C ₆ H ₅ SeCH(CH ₃)CHO CH ₃ COCH(OCH ₃)- SC ₆ H ₅ CH ₃ COCH=CH- Si(CH ₃) ₃ C ₂ H ₅ COCH=CH- Si(CH ₃) ₃ <i>t</i> -C ₄ H ₉ CHO <i>i</i> -C ₃ H ₇ CH(SeC ₆ H ₅)CHO Cyclohexanone	Li Mg, Et ₂ O, 0° Mg, Et ₂ O " " Li Mg, Et ₂ O	(CH ₃) ₃ SiCH ₂ CHOHCH(CH ₃)SeC ₆ H ₅ (85) (CH ₃) ₃ SiCH ₂ C(CH ₃)OHCH(OCH ₃)SC ₆ H ₅ (~90) (CH ₃) ₃ SiCH ₂ C(CH ₃)OHCH=CHSi(CH ₃) ₃ (95) (CH ₃) ₃ SiCH ₂ C(C ₂ H ₅)OHCH=CHSi(CH ₃) ₃ (65) (CH ₃) ₃ SiCH ₂ CHOHC ₄ H ₉ - <i>t</i> (73) (CH ₃) ₃ SiCHOHCH(SeC ₆ H ₅)C ₃ H ₇ - <i>i</i> (75) (CH ₃) ₃ SiCH ₂ OH (86)	412 108 (~90) 119 (95) 119 (65) 4 412 4



TABLE II. FORMATION OF β -HYDROXSILANES (Continued)

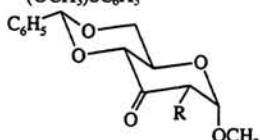
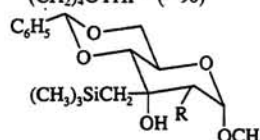
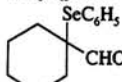
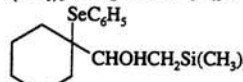
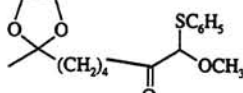
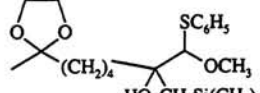
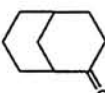
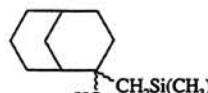
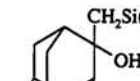
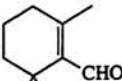





Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	R	R ¹	R ²				
				<i>i</i> -C ₃ H ₇ COCH=CH-Si(CH ₃) ₃	"	(CH ₃) ₃ SiCH ₂ COH(C ₃ H ₇ - <i>i</i>)CH=CHSi(CH ₃) ₃ (85)	119
				<i>n</i> -C ₄ H ₉ CH(SeC ₆ H ₅)-CHO	Li	(CH ₃) ₃ SiCH ₂ CHOHCH(SeC ₆ H ₅)C ₄ H ₉ - <i>n</i> (84)	412
				(C ₂ H ₅) ₂ C(SeC ₆ H ₅)CHO	"	(CH ₃) ₃ SiCH ₂ CHOHC(SeC ₆ H ₅)(C ₂ H ₅) ₂ (92)	412
				THPO(CH ₂) ₄ COCH(OCH ₃)SC ₆ H ₅	Mg, Et ₂ O	(CH ₃) ₃ SiCH ₂ COH[CH(OCH ₃)(SC ₆ H ₅)]-(CH ₂) ₄ OTHP (~90)	108
							454
				R = H	"	R = H (90)	
				R = O ₂ CC ₆ H ₅	"	R = O ₂ CC ₆ H ₅ (87)	454
				C ₆ H ₅ CHO	"	(CH ₃) ₃ SiCH ₂ CHOHC ₆ H ₅ (83)	3, 4
				<i>n</i> -C ₆ H ₁₃ CHO	"	(CH ₃) ₃ SiCH ₂ CHOHC ₆ H ₁₃ - <i>n</i> (84)	4
					Li		412
				C ₆ H ₅ CH ₂ CHO	Mg, Et ₂ O	(CH ₃) ₃ SiCHOHCH ₂ C ₆ H ₅ (35)	4
				<i>n</i> -C ₇ H ₁₅ CHO	"	(CH ₃) ₃ SiCH ₂ CHOHC ₇ H ₁₅ - <i>n</i> (-)	3
					"		(~90) 108
				C ₆ H ₅ CH ₂ CH(SeC ₆ H ₅)-CHO	Li	(CH ₃) ₃ SiCH ₂ CHOHCH(SeC ₆ H ₅)CH ₂ C ₆ H ₅ (68)	412
					Mg, Et ₂ O		(70) 117
				C ₆ H ₅ COCH=CH-Si(CH ₃) ₃	"	(CH ₃) ₃ SiCH ₂ C(C ₆ H ₅)OHCH=CHSi(CH ₃) ₃ (90)	119
				Adamantanone	"		(89) 4
					"		(-) 122
				HC≡C(CH ₂) ₃ -C≡C(CH ₂) ₂ CHO	"	(CH ₃) ₃ SiCH ₂ CHOH(CH ₂) ₃ C≡C(CH ₂) ₂ -C≡CH (80)	140
					1. Mg, THF 2. AcCl		(87) 107
					1. Mg, THF 2. NH ₄ Cl, H ₂ O		(61) 107
				(C ₆ H ₅) ₂ CO	Mg, Et ₂ O	(CH ₃) ₃ SiCH ₂ COH(C ₆ H ₅) ₂ (-)	3
				<i>n</i> -C ₁₁ H ₂₃ COCH(OCH ₃)SC ₆ H ₅	"	(CH ₃) ₃ SiCH ₂ COH(C ₁₁ H ₂₃ - <i>n</i>)CH(OCH ₃)-SC ₆ H ₅ (~90)	108

TABLE II. FORMATION OF β -HYDROXYSILANES (Continued)

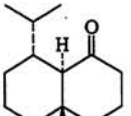
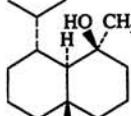
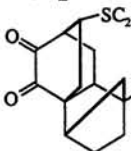
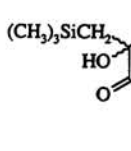
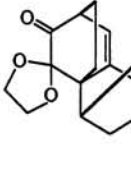
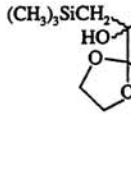
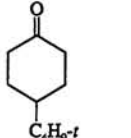
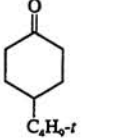
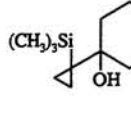
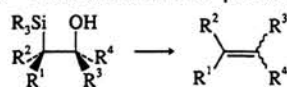
	Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	X	R	R ¹	R ²				
						Mg, THF, heat, 18 h	 (—)	116
						Mg, THF	 (75)	112
						"	 (80)	111
	Ti(OC ₃ H ₇ - <i>i</i>) ₃	CH ₃	H	H	C ₆ H ₅ CHO	THF, 48 h	(CH ₃) ₃ SiCH ₂ CHOHC ₆ H ₅ (41)	147
C ₂	SeCH ₃	C ₂ H ₅	CH ₃	H	C ₆ H ₅ COCH ₂ C ₆ H ₅	<i>n</i> -C ₄ H ₉ Li, THF, 0°	(CH ₃) ₃ SiCOH(C ₆ H ₅)CH ₂ C ₆ H ₅ (20)	165
	SeCH ₃	CH ₃	—(CH ₂) ₂ —	H	<i>n</i> -C ₃ H ₇ CH=CHCHO	<i>n</i> -C ₄ H ₉ Li	(CH ₃) ₃ Si CHOHC ₃ H ₇ - <i>n</i> (72)	143
					<i>n</i> -C ₆ H ₁₃ CH(SeCH ₃)-CHO	"	(CH ₃) ₃ Si CHOH(SeCH ₃)CHC ₆ H ₁₃ - <i>n</i> (60)	143
					<i>n</i> -C ₁₀ H ₂₁ CHO	"	(CH ₃) ₃ Si CHOHC ₁₀ H ₂₁ - <i>n</i> (85)	143
					<i>n</i> -C ₉ H ₁₉ COCH ₃		(CH ₃) ₃ Si COH(CH ₃)C ₉ H ₁₉ - <i>n</i> (40)	143
C ₃	SC ₆ H ₅	CH ₃	C ₂ H ₅	H	CH ₃ CHO	LDMAN, THF, -45°	(CH ₃) ₃ SiCH(C ₂ H ₅)CHOHCH ₃ (65)	155
						"	HO CH(C ₂ H ₅)Si(CH ₃) ₃ (30)	155
	SC ₆ H ₅	CH ₃	CH ₃	CH ₃	C ₆ H ₁₁ CHO	"	(CH ₃) ₃ SiC(CH ₃) ₂ CHOHC ₆ H ₁₁ (79)	155
	SC ₆ H ₅	CH ₃	—(CH ₂) ₂ —	CH ₃	<i>p</i> -CH ₃ OC ₆ H ₄ CHO	"	(CH ₃) ₃ Si CHOHC ₆ H ₄ OCH ₃ - <i>p</i> (85)	155
					<i>n</i> -C ₆ H ₁₃ CHO	"	(CH ₃) ₃ Si CHOHC ₆ H ₁₃ - <i>n</i> (84)	155
						"	(CH ₃) ₃ Si  (86)	155
C ₄	Li	CH ₃	<i>n</i> -C ₃ H ₇	H	<i>n</i> -C ₃ H ₇ CHO	C ₂ H ₅ Li, CH ₂ =CHSi(CH ₃) ₃	(CH ₃) ₃ SiCH(C ₃ H ₇ - <i>n</i>)CHOHC ₃ H ₇ - <i>n</i> (—)	26
C ₅	SeCH ₃	CH ₃	—[CH(CH ₃)] ₂ —		<i>n</i> -C ₃ H ₇ CH=CHCHO	<i>n</i> -C ₄ H ₉ Li	(CH ₃) ₃ Si CHOHC ₃ H ₇ - <i>n</i> (72)	143
					<i>n</i> -C ₅ H ₁₁ CHO	"	(CH ₃) ₃ Si CHOHC ₅ H ₁₁ - <i>n</i> (70)	143

TABLE II. FORMATION OF β -HYDROXYSILANES (Continued)

Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	R	R ¹	R ²				
				$n\text{-C}_{10}\text{H}_{21}\text{CHO}$	"	(CH ₃) ₃ Si-CHOHC ₁₀ H _{21-n} (71)	143
SeCH ₃	CH ₃	—[CH(CH ₃)] ₂ —		$n\text{-C}_3\text{H}_7\text{CH}=\text{CHCHO}$	"	(CH ₃) ₃ Si-CHOHCH=CHC ₃ H _{7-n} (59)	143
				$n\text{-C}_6\text{H}_{13}\text{CH}(\text{SeCH}_3)\text{CHO}$	"	(CH ₃) ₃ Si-CHOH(SeCH ₃)C ₆ H _{13-n} (59)	143
C ₆	SC ₆ H ₅	CH ₃	—(CH ₂) ₅ —	C ₆ H ₁₁ CHO	LDMAN, THF, -45°	(CH ₃) ₃ Si-CHOHC ₆ H ₁₁ (51)	155
				CH ₃ C(=CH ₂)CHO	"	CHOHC(CH ₃)=CH ₂ (91) Si(CH ₃) ₃	155
C ₇				"	"	CHOHC(CH ₃)=CH ₂ (90) Si(CH ₃) ₃	155
				$n\text{-C}_5\text{H}_{11}\text{CHO}$	"	CHOHC ₅ H _{11-n} (92) Si(CH ₃) ₃	155
				$p\text{-CH}_3\text{OC}_6\text{H}_4\text{CHO}$	"	CHOHC ₆ H ₄ CH _{3-p} (92) Si(CH ₃) ₃	155
CH ₃ Se CH ₃ Se	CH ₃ C ₂ H ₅	$n\text{-C}_6\text{H}_{13}$ $n\text{-C}_6\text{H}_{13}$	H H	$n\text{-C}_6\text{H}_{13}\text{CHO}$	$n\text{-C}_4\text{H}_9\text{Li}$, THF, 0°, 1 h	(CH ₃) ₃ SiCH(C ₆ H _{13-n})CH-OHC ₆ H _{13-n} (50)	165
				"	"	" (30)	165
				Cyclohexanone	"	HO-CH(C ₆ H _{13-n})Si(CH ₃) ₃ (30)	165
				$n\text{-C}_3\text{H}_7\text{CH}=\text{CHCHO}$	$n\text{-C}_4\text{H}_9\text{Li}$	CHOHCH=CHC ₃ H _{7-n} (10) Si(CH ₃) ₃	143
				$n\text{-C}_5\text{H}_{11}\text{CHO}$	"	CHOHC ₅ H _{11-n} (40) Si(CH ₃) ₃	143
C ₁₀	(CH ₃) ₃ Si SC ₆ H ₅			C ₆ H ₁₁ CHO	LDMAN, THF, -45°	(CH ₃) ₃ Si-CHOHC ₆ H ₁₁ (58)	155
						C ₄ H _{9-t}	

TABLE III. ELIMINATIONS OF β -HYDROXYSILANES


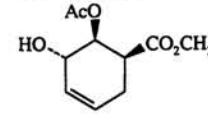
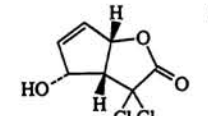
Silane					Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
R	R ¹	R ²	R ³	R ⁴			
C ₂							
CH ₃	HC≡C-(CH ₂) _n O n = 1 n = 2 n = 3	H	H	H	KH, Et ₂ O, 0°	HC≡C(CH ₂) _n CH=CH ₂ n = 1 (50) n = 2 (55) n = 3 (72)	70
CH ₃	HC≡C(CH ₂) _n -CO ₂ n = 0 n = 2 n = 8	H	H	H	1. C ₆ H ₁₁ N=COAc C ₆ H ₁₁ NH ⁺ 2. (C ₄ H ₉) ₄ NF ⁻	HC≡C(CH ₂) _n CO ₂ CH=CH ₂ n = 0 (56) n = 2 (69) n = 8 (76)	70
C ₃							
CH ₃	H	H	CH ₃	H	H ₂ SO ₄	CH ₂ =CHCH ₃ (—) ^a	2
C ₄							
CH ₃	H	H	CH ₃	CH ₃	KOC ₄ H ₉ -t, THF	CH ₂ =C(CH ₃) ₂ (35) ^a	3
CH ₃	H	H	CH ₃	CH(OCH ₃)SC ₆ H ₅	NaH, HMPA, THF	CH ₂ =C(CH ₃)CH(OCH ₃)SC ₆ H ₅ (~80)	108
CH ₃	H	H	H	CH(CH ₃)SeC ₆ H ₅	SnCl ₂ , CH ₂ Cl ₂	CH ₃ CH=CHCH ₂ SeC ₆ H ₅ (63)	412
CH ₃	H	COFe(CO)(C ₂ H ₅)- [P(C ₆ H ₅) ₃]	H	CH ₃	NaH, THF	[(C ₆ H ₅) ₃ P](C ₂ H ₅)(CO)FeCO-CH=CHCH ₃ (—)	51
TBDM	H	H	H	CH ₂ CO ₂ C ₄ H ₉ -t	BF ₃ ·OEt ₂ , CH ₂ Cl ₂	CH ₂ =CHCH ₂ CO ₂ C ₄ H ₉ -t (64)	58
C ₅							
CH ₃	H	H	CH ₃	CH ₂ CO ₂ C ₄ H ₉ -t	HClO ₄ , THF, 0°	CH ₂ =C(CH ₃)CH ₂ CO ₂ C ₄ H ₉ -t (65)	60
CH ₃	H	H	CH ₃	CH ₂ CON(CH ₃) ₂	"	CH ₂ =C(CH ₃)CH ₂ CON(CH ₃) ₂ (75)	60
C ₆							
CH ₃	H	H	H	C ₄ H ₉ -n	KH, THF	CH ₂ =CHC ₄ H ₉ -n (95) ^b	72
CH ₃	H	H	H	CH(C ₂ H ₇ -n)NHC ₆ H ₅	Acid or base ^c	CH ₂ =CHCH(C ₂ H ₇ -n)NHC ₆ H ₅ (87)	456
CH ₃	H	H	H	CH(C ₂ H ₇ -i)SeC ₆ H ₅	SnCl ₂ , CH ₂ Cl ₂	<i>i</i> -C ₂ H ₇ CH=CHCH ₂ SeC ₆ H ₅ (86)	412
C ₇							
CH ₃	H	H	H	(CH ₂) ₄ CO ₂ H	BF ₃ ·OEt ₂	CH ₂ =CH(CH ₂) ₄ CO ₂ H (86)	86
CH ₃	H	H	CH(OCH ₃)SC ₆ H ₅	(CH ₂) ₄ OTHP	NaH, HMPA, THF	CH ₂ =C[(CH ₂) ₄ OTHP]CH(OCH ₃)SC ₆ H ₅ (~80)	108
CH ₃	(CH ₂) ₃ CO ₂ H	H	CH ₃	H	BF ₃ ·OEt ₂	CH ₃ CH=CH(CH ₂) ₃ CO ₂ H (81)	86
CH ₃	CH ₃	H	(CH ₂) ₃ CO ₂ H	H	"	" (63)	86
					KH, THF	" (62)	86
					TsOH, C ₆ H ₆ , heat	E:Z = 3.5:96.5 (94)	79
							
					H ₂ SO ₄ , 1 h	(73)	33
							
CH ₃	H	H	H	C(C ₂ H ₅) ₂ SeC ₆ H ₅	SnCl ₂ , CH ₂ Cl ₂	(C ₂ H ₅) ₂ C=CHCH ₂ SeC ₆ H ₅ (20) + (C ₂ H ₅) ₂ C(CHO)CH ₂ Si(CH ₃) ₃ (46)	412
CH ₃	H	H	H	CH(C ₄ H ₉ -n)SeC ₆ H ₅	"	<i>n</i> -C ₄ H ₉ CH=CHCH ₂ SeC ₆ H ₅ (63)	412

TABLE III. ELIMINATIONS OF β-HYDROXYSILANES (Continued)

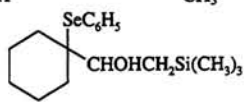
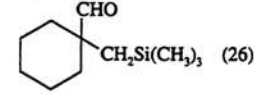
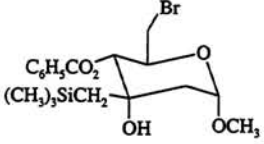
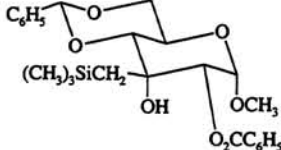
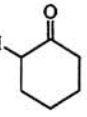
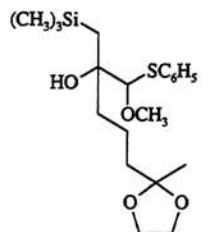
	Silane					Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	R	R ¹	R ²	R ³	R ⁴			
C ₈	CH ₃	H	H	CH ₃	<i>n</i> -C ₅ H ₁₁	NaOAc, AcOH	CH ₂ =C(CH ₃)C ₅ H ₁₁ - <i>n</i> (90)	55
	CH ₃	H	H	C ₆ H ₅	H	KH, THF	CH ₂ =CHC ₆ H ₅ (91) ^d	3
						H ₂ SO ₄ , THF	" (-) ^d	3
	CH ₃	H	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇	H	KH, THF	<i>n</i> -C ₃ H ₇ CH=CHC ₃ H ₇ - <i>n</i> (96) ^e	26, 27
						NaH, HMPA	" <i>E</i> : <i>Z</i> = 95:5	(85) ^e 26, 27
						H ₂ SO ₄ , THF	" <i>E</i> : <i>Z</i> = 93:3	(99) ^e 26, 27
						BF ₃ ·OEt ₂ , CH ₂ Cl ₂	" <i>E</i> : <i>Z</i> = 8:92	(99) ^e 26, 27
						CH ₃ SO ₂ Cl, NEt ₃ , C ₅ H ₁₂	" <i>E</i> : <i>Z</i> = 6:94	(80) ^e 26, 27
						NaOAc, Ac ₂ O, DMSO	" <i>E</i> : <i>Z</i> = 11:89	(81) ^e 26, 27
						NaOAc, AcOH, 50°	" <i>E</i> : <i>Z</i> = 13:87	(85) ^e 27
120	CH ₃	<i>n</i> -C ₃ H ₇	H	<i>n</i> -C ₃ H ₇	H	KH, THF	" <i>E</i> : <i>Z</i> = 2:98	(98) ^e 72, 73
						BF ₃ ·OEt ₂ , CH ₂ Cl ₂	" <i>E</i> : <i>Z</i> = 2:98	(102) ^e 72, 73
						H ₂ SO ₄ , THF	" <i>E</i> : <i>Z</i> = 98:2	(96) ^e 72
							" <i>E</i> : <i>Z</i> = 99:1	
121	CH ₃	<i>n</i> -C ₄ H ₉	H	CH ₃	CH ₃	NaOAc, AcOH SnCl ₂ , CH ₂ Cl ₂	<i>n</i> -C ₄ H ₉ CH=C(CH ₃) ₂ (81)  (16) +  (26)	72 412
121						1. NaOCH ₃ , CH ₃ OH 2. H ₃ O ⁺	 (95)	4
						KH, THF, heat	 (58)	4
	TBDM	H	H	H	<i>n</i> -C ₆ H ₁₃	KH, THF	CH ₂ =CHCH ₂ C ₆ H ₁₃ - <i>n</i> (-)	58
	TBDM	H	H	H	CH ₂ COC ₄ H ₉ - <i>t</i>	BF ₃ ·OEt ₂ , CH ₂ Cl ₂	" (-) CH ₂ =CHCH ₂ COC ₄ H ₉ - <i>t</i> (65)	58 58
						"	CH ₂ =CH-  (49)	58
C ₉	CH ₃	H	H	H	<i>n</i> -C ₇ H ₁₅	KH, THF	CH ₂ =CHC ₇ H ₁₅ - <i>n</i> (70)	3
	CH ₃	H	H	H	CH(C ₆ H ₅)NHCH ₃	H ₂ SO ₄ , THF	" (73)	3
						Acid or base ^e	CH ₂ =CH(C ₆ H ₅)NHCH ₃ (72)	456
						NaH, HMPA, THF	 (~80)	108

TABLE III. ELIMINATIONS OF β -HYDROXYSILANES (Continued)


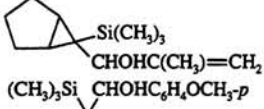
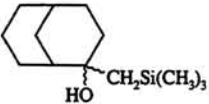
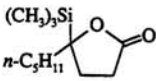

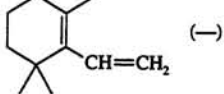

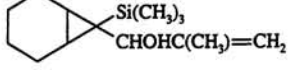
	Silane					Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	R	R ¹	R ²	R ³	R ⁴			
	CH ₃	<i>n</i> -C ₄ H ₉	H	<i>n</i> -C ₄ H ₉	H	KH, THF	<i>n</i> -C ₄ H ₉ CH=CHC ₄ H ₉ - <i>n</i> <i>E:Z</i> = 4:96	(82) 457
						BF ₃ ·OEt ₂	" <i>E:Z</i> = 95:5	(85) 457
	CH ₃	C ₆ H ₁₁	H	C ₂ H ₅	H	"	C ₆ H ₁₁ CH=CHC ₂ H ₅ <i>E:Z</i> = 97:3	(90) 72
						KH, THF	" <i>E:Z</i> = 2:98	(90) 72
C ₁₀	CH ₃	CH ₃	CH ₃	H	C ₆ H ₁₁	KH, diglyme, 90° KH, THF	(CH ₃) ₂ C=CHC ₆ H ₁₁ (92) 	(95) 155 155
						KH, THF, 90°	CHC ₆ H ₄ OCH ₃ - <i>p</i> (90)	155
						NaH, THF, 150°, 10 h	(65)	117
	CH ₃	H	H	C ₆ H ₅	CH ₂ CO ₂ C ₄ H ₉ - <i>t</i>	HClO ₄ , THF, 0°	CH ₂ =C(C ₆ H ₅)CH ₂ CO ₂ C ₄ H ₉ - <i>t</i> (65)	60
	CH ₃	H	H	C ₆ H ₁₁	CH ₂ CO ₂ C ₄ H ₉ - <i>t</i>	"	CH ₂ =C(C ₆ H ₁₁)CH ₂ CO ₂ C ₄ H ₉ - <i>t</i> (77)	60
	CH ₃	H	H	C ₆ H ₁₁	CH ₂ CON(CH ₃) ₂	"	CH ₂ =C(C ₆ H ₁₁)CH ₂ CON(CH ₃) ₂ (60)	60
						1. AC ₂ O, py 2. (C ₄ H ₉) ₄ NF	<i>n</i> -C ₃ H ₁₁ CH=CHC ₂ H ₃ O <i>E:Z</i> = 99:1	(72) 339
	CH ₃	H	H	H	CH(CH ₂ C ₆ H ₅)Se-C ₆ H ₅	SnCl ₂ , CH ₂ Cl ₂	C ₆ H ₅ CH ₂ CH=CHCH ₂ SeC ₆ H ₅ (57)	412
	TBDM	<i>n</i> -C ₆ H ₁₃	H	C ₂ H ₅	H	BF ₃ ·OEt ₂ , CH ₂ Cl ₂	<i>n</i> -C ₆ H ₁₃ CH=CHC ₂ H ₅ <i>E:Z</i> = 95-99.5:5-0.5 ^f	(84-89) 58
						KH, THF	" <i>E:Z</i> = 6-1:94-99 ^f	(72-79) 58
C ₁₁	CH ₃	H	H	H	(CH ₂) ₂ C=C(CH ₂) ₃ -C≡CH	"	CH ₂ =CH(CH ₂) ₂ C=C(CH ₂) ₃ -C≡CH (68) + CH ₂ =CH-(CH ₂) ₂ C=C(CH ₂) ₂ C≡CCH ₃ (17)	140
						TsOH, H ₂ SO ₄	 (—)	122
			(CH ₃) ₃ Si-CHOHCH=CHC ₃ H ₇ - <i>n</i>			KH, THF	CHCH=CHC ₃ H ₇ - <i>n</i> (76)	143
						"	CH=CHC ₃ H ₇ - <i>n</i> (71)	143
						"	CHC(CH ₃)=CH ₂ (100)	155
C ₁₂	CH ₃	CH ₃ Se	H	<i>n</i> -C ₁₀ H ₂₁	H	KOC ₄ H ₉ - <i>t</i> , THF, 55°	CH ₃ SeCH=CHC ₁₀ H ₂₁ - <i>n</i> <i>E:Z</i> ~ 0:100	(74) 257
	CH ₃	CH ₃ Se	H	H	<i>n</i> -C ₁₀ H ₂₁	"	" <i>E:Z</i> ~ 100:0	(78) 257

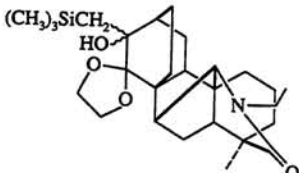
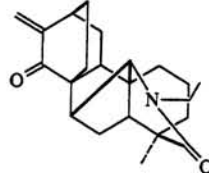
TABLE III. ELIMINATIONS OF β -HYDROXYSILANES (Continued)

Silane					Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
R	R ¹	R ²	R ³	R ⁴			
					BF ₃ ·OEt ₂ , CH ₂ Cl ₂	(—)	107
					CF ₃ CO ₂ H, THF, heat	" (—)	107
					KH, THF	(100)	143
					"	(88)	143
					"	(85)	155
					"	(83)	155
					KH, diglyme, 90°	(86)	155
					KH, diglyme	=CHC ₃ H _{11-n} (98)	155
					KH, THF, -78°	(50) + 36	36
					"	(20) + 36	36
					"	(86) + 36	36
					"	(16) + 36	36

TABLE III. ELIMINATIONS OF β -HYDROXYSILANES (Continued)

		Silane				Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
R	R ¹	R ²	R ³	R ⁴				
						"	(87) + 36	
CH ₃	CH ₃ Se	H	<i>n</i> -C ₁₀ H ₂₁	H	KOC ₄ H ₉ - <i>t</i> , THF	(13)		
CH ₃	CH ₃ Se	H	H	<i>n</i> -C ₁₀ H ₂₁	"	CH ₃ SeCH=CHC ₁₀ H ₂₁ - <i>n</i> E:Z ~ 0:100 (89)	257	
						"	E:Z ~ 100:0 (70)	257
C ₁₄	CH ₃	H	H	C ₆ H ₅	C ₆ H ₅	KH, THF NaH, THF 1. SOCl ₂ , Δ 2. (C ₄ H ₉) ₄ NF	CH ₂ =C(C ₆ H ₅) ₂ (86) " (67) ^f n-C ₁₀ H ₂₁ - <i>n</i> (46)	3 3 143
						KH, THF "	" (0) CHC ₆ H ₄ OCH ₃ - <i>p</i> (95) ^A	143 155
CH ₃	H	H	<i>n</i> -C ₁₁ H ₂₃	CH(OCH ₃)SC ₆ H ₅	NaH, HMPA, THF	CH ₂ =C(C ₁₁ H ₂₃ - <i>n</i>)CH(OCH ₃)S-C ₆ H ₅ (~80)	108	
TBDM	<i>n</i> -C ₆ H ₁₃	H	CH ₂ COC ₄ H ₉ - <i>t</i>	H	BF ₃ ·OEt ₂ , CH ₂ Cl ₂	<i>n</i> -C ₆ H ₁₃ CH=CHCH ₂ COC ₄ H ₉ - <i>t</i> E:Z ~ 100:0 (68)	58	
TBDM	<i>n</i> -C ₆ H ₁₃	H	CH ₂ CHOH	C ₄ H ₉ - <i>t</i>	"	<i>n</i> -C ₆ H ₁₃ CH=CHCH ₂ CHOH-C ₄ H ₉ - <i>t</i> E:Z ~ 100:0 (-)	58	
					KH, THF	" E:Z ~ 0:100 (-)	(-) 58	
C ₁₅						KH	(97) 458 ^f	
						AcOH, H ₂ O	(40) 116	
						HClO ₄ , H ₂ O, THF	(90) 112	
C ₁₇						BF ₃ ·OEt ₂ , CH ₂ Cl ₂ , 0°	(>86) ^f 83	
						KH, THF	(80) 155	

TABLE III. ELIMINATIONS OF β -HYDROXYSILANES (Continued)

R	Silane				Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	R ¹	R ²	R ³	R ⁴			
C ₁₉					HClO ₄ , THF	 (100)	111

^a The alkene is isolated as the dibromide.

^b The yield is determined by VPC analysis.

^c No specific conditions are given.

^d The product is isolated as polystyrene.

^e The yield is determined by GLC.

^f The exact yield and isomer distribution depend on the method used for the preparation of the β -hydroxysilane.

^g The yield is determined by NMR and GLC.

^h The product is obtained as a mixture of isomers.

ⁱ For closely related eliminations see references 459 and 460.

TABLE IV. REACTIONS OF SILANES CONTAINING UNSATURATION WITHOUT ISOLATION OF A β -HYDROXYSILANE

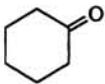
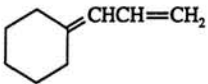
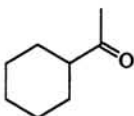
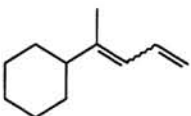
Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 $(C_6H_5)_3SiCBr=CH_2$	C_6H_5CHO	1. $n-C_4H_9Li$ 2. $SOCl_2$ 3. $(C_2H_5)_4N^+F^-$, DMSO	$C_6H_5CH=C=CH_2$ (59)	171
	$n-C_{10}H_{21}CHO$	"	$n-C_{10}H_{21}CH=C=CH_2$ (44)	171
	$C_6H_5CH=CHCHO$	"	$C_6H_5CH=CHCH=C=CH_2$ (35)	171
	$(C_6H_5)_2CO$	"	$(C_6H_5)_2C=C=CH_2$ (45)	171
C_3 $(CH_3)_3SiCH_2CH=CH_2$		1. $t-C_4H_9Li$, HMPA, 0° 2. $MgBr_2$ 3. Carbonyl compound 4. $SOCl_2$	 (49)	176
	C_6H_5CHO	"	$C_6H_5CH=CHCH=CH_2$ (50)	176
	$C_6H_{11}CHO$	1. $t-C_4H_9Li$, HMPA, 0° 2. $MgBr_2$ 3. Carbonyl compound 4. $SOCl_2$	$C_6H_{11}CH=CHCH=CH_2$ (42)	176
	$C_6H_5COCH_3$	1. $t-C_4H_9Li$, HMPA, 0° 2. $MgBr_2$ 3. Carbonyl compound 4. $SOCl_2$	$C_6H_5(CH_3)C=CHCH=CH_2$ (43)	176
		$s-C_4H_9Li$, THF	 (5)	174

TABLE IV. REACTIONS OF SILANES CONTAINING UNSATURATION WITHOUT ISOLATION OF A β -HYDROXYSILANE (Continued)



Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$n\text{-C}_{10}\text{H}_{21}\text{CHO}$	1. $t\text{-C}_4\text{H}_9\text{Li}$, HMPA, 0° 2. MgBr_2 3. Carbonyl compound 4. SOCl_2	$n\text{-C}_{10}\text{H}_{21}\text{CH}=\text{CHCH}=\text{CH}_2$ (54)	176
$(\text{CH}_3)_3\text{SiCH}=\text{CHCH}_2\text{Si}(\text{CH}_3)_3$	HCHO		$\text{CH}_2=\text{CHCH}=\text{CHSi}(\text{CH}_3)_3$ (10)	103
	$n\text{-C}_3\text{H}_7\text{CHO}$	$s\text{-C}_4\text{H}_9\text{Li}$, THF, -78° or $t\text{-C}_4\text{H}_9\text{Li}$, THF, HMPA	$n\text{-C}_3\text{H}_7\text{CH}=\text{CHCH}=\text{CHSi}(\text{CH}_3)_3$ $1E, 3E:1E, 3Z = 60:40^a$	(34) 28
	$\text{C}_6\text{H}_5\text{CHO}$	"	$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{CHSi}(\text{CH}_3)_3$ $1E, 3E:1E, 3Z:1Z, 3E = 77:20:3^a$	(77) 28
	$n\text{-C}_8\text{H}_{17}\text{CHO}$	"	$n\text{-C}_8\text{H}_{17}\text{CH}=\text{CHCH}=\text{CHSi}(\text{CH}_3)_3$ $1E, 3E:1E, 3Z:1Z, 3E = 73:24:3^a$	(27) 28
$(\text{CH}_3)_3\text{SiCH}=\text{CHCH}_2\text{Si}(\text{C}_6\text{H}_5)_3$ $(\text{CH}_3)_3\text{SiC}\equiv\text{CCH}_2\text{Si}(\text{CH}_3)_3$	$(\text{C}_6\text{H}_5)_2\text{CO}$	$\text{C}_6\text{H}_5\text{Li}$, Et_2O , TMEDA $n\text{-C}_4\text{H}_9\text{Li}$	$(\text{C}_6\text{H}_5)_3\text{SiCH}=\text{CHCH}=\text{C}(\text{C}_6\text{H}_5)_2$ (>95)  (83)	173 82
	"	1. $n\text{-C}_4\text{H}_9\text{Li}$ 2. MgBr_2	" (88)	82
	$n\text{-C}_5\text{H}_{11}\text{CHO}$	"	$n\text{-C}_5\text{H}_{11}\text{CH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ $E:Z = 1:7^b$	(75) 82
	"	$n\text{-C}_4\text{H}_9\text{Li}$	" $E:Z = 1:3^b$	(77) 82
	$\text{C}_6\text{H}_5\text{CHO}$	"	$\text{C}_6\text{H}_5\text{CH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ $E:Z = 1:1^b$	(53) 82
	"	1. $n\text{-C}_4\text{H}_9\text{Li}$ 2. MgBr_2	" $E:Z = 1:3^b$	(76) 82
	$\text{C}_6\text{H}_{11}\text{CHO}$	"	$\text{C}_6\text{H}_{11}\text{CH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ $E:Z = 1:20^b$	(84) 82
	"	$n\text{-C}_4\text{H}_9\text{Li}$	" $E:Z = 1:8^b$	(69) 82
	$\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$	1. $n\text{-C}_4\text{H}_9\text{Li}$ 2. MgBr_2	$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ $E:Z = 1:2^b$	(88) 82
$(\text{CH}_3)_3\text{SiC}\equiv\text{CCH}_2\text{Si}(\text{C}_2\text{H}_5)_3$	Cyclohexanone	"	 $\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ (93)	82
	$n\text{-C}_3\text{H}_7\text{CHO}$	"	$n\text{-C}_3\text{H}_7\text{CH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ $E:Z = 1:31^b$	(89) 82
	"	$n\text{-C}_4\text{H}_9\text{Li}$	" $E:Z = 1:6^b$	(78) 82
	$\text{C}_6\text{H}_5\text{CHO}$	"	$\text{C}_6\text{H}_5\text{CH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ $E:Z = 1:1^b$	(63) 82
	"	1. $n\text{-C}_4\text{H}_9\text{Li}$ 2. MgBr_2	" $E:Z = 2:1^b$	(78) 82
	$\text{C}_6\text{H}_{11}\text{CHO}$	"	$\text{C}_6\text{H}_{11}\text{CH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ $E:Z = 1:23^b$	(96) 82
	"	$n\text{-C}_4\text{H}_9\text{Li}$	" $E:Z = 1:10^b$	(88) 82
$(\text{CH}_3)_3\text{SiC}\equiv\text{CCH}_2\text{Si}(\text{CH}_3)_2$ $\text{C}_4\text{H}_9\text{-}t$	$n\text{-C}_3\text{H}_7\text{CHO}$	1. $n\text{-C}_4\text{H}_9\text{Li}$ 2. MgBr_2	$n\text{-C}_3\text{H}_7\text{CH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ $E:Z < 1:50^b$	(65) 82
	$\text{C}_6\text{H}_5\text{CHO}$	"	$\text{C}_6\text{H}_5\text{CH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ $E:Z = 1:1$	(55) 82
	$\text{C}_6\text{H}_{11}\text{CHO}$	"	$\text{C}_6\text{H}_{11}\text{CH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ $E:Z = 1:12^b$	(55) 82
	"	$n\text{-C}_4\text{H}_9\text{Li}$	" $E:Z = 1:30^b$	(75) 82
	$\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$	1. $n\text{-C}_4\text{H}_9\text{Li}$ 2. MgBr_2	$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ $E:Z = 1:7$	(90) 82
$(i\text{-C}_3\text{H}_7)_3\text{SiC}\equiv\text{CCH}_2\text{Si}(\text{C}_3\text{H}_7\text{-}i)_3$	$t\text{-C}_4\text{H}_9\text{CHO}$	$n\text{-C}_4\text{H}_9\text{Li}$, THF, -20°	$t\text{-C}_4\text{H}_9\text{CH}=\text{CHC}\equiv\text{CSi}(\text{C}_3\text{H}_7\text{-}i)_3$ $E:Z > 1:20$	(79) 179
	"	1. $n\text{-C}_4\text{H}_9\text{Li}$, THF, -20° 2. HMPA, -78°	" $E:Z = 20\text{-}10:1$	(60-65) 179
	$n\text{-C}_6\text{H}_{13}\text{CHO}$	$n\text{-C}_4\text{H}_9\text{Li}$, THF, -20°	$n\text{-C}_6\text{H}_{13}\text{CH}=\text{CHC}\equiv\text{CSi}(\text{C}_3\text{H}_7\text{-}i)_3$ $E:Z > 1:20$	(57) 179
	"	1. $n\text{-C}_4\text{H}_9\text{Li}$, THF, -20° 2. HMPA, -78°	" $E:Z = 20\text{-}10:1$	(60-65) 179

TABLE IV. REACTIONS OF SILANES CONTAINING UNSATURATION WITHOUT ISOLATION OF A β -HYDROXYSILANE (Continued)

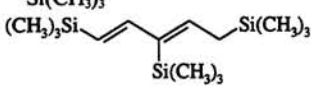
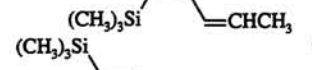
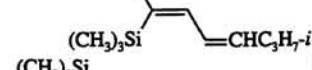
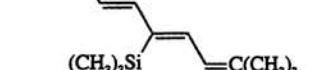
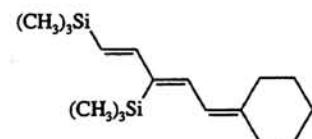
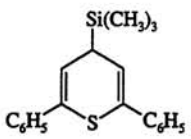
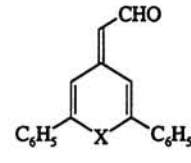
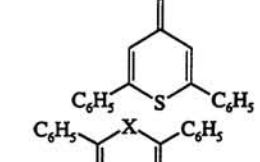
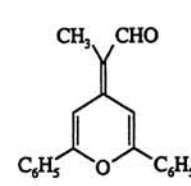
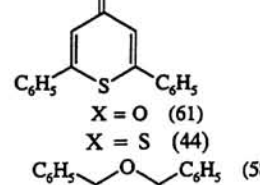
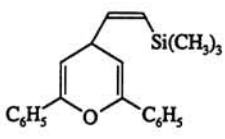
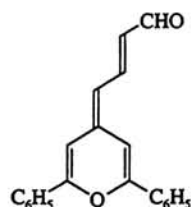
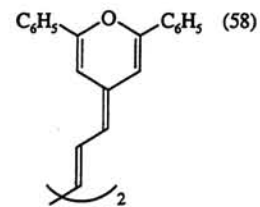
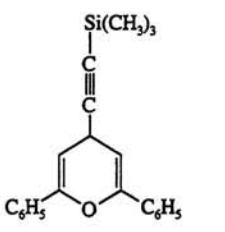

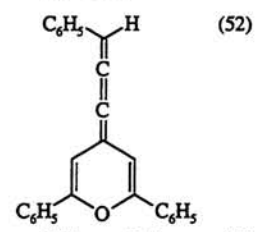


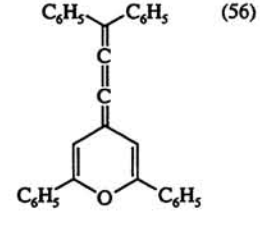

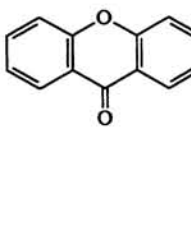
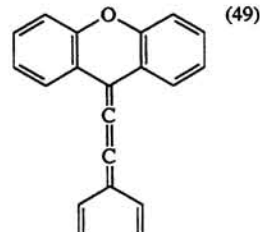

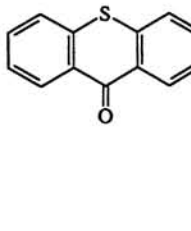
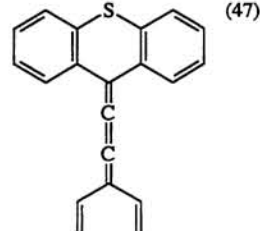

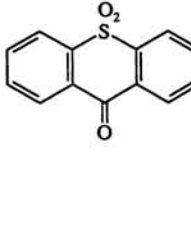
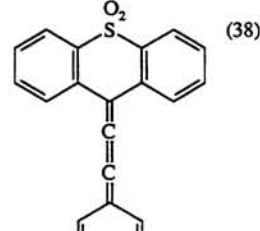
Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$C_6H_{13}CHO$	$n-C_4H_9Li$, THF, -20°	$C_6H_{13}CH=CHC\equiv Si(C_3H_7-i)_3$ (71) $E:Z > 1:20$	179
	"	1. $n-C_4H_9Li$, THF, -20° 2. HMPA, -78°	" (60-65) $E:Z = 20-10:1$	179
	C_6H_5CHO	"	$C_6H_5CH=CHC\equiv Si(C_3H_7-i)_3$ (60-65) $E:Z = 9:1$	179
	$p-CH_3OC_6H_4CHO$	"	$p-CH_3OC_6H_4CH=CHC\equiv Si(C_3H_7-i)_3$ (60-65) $E:Z = 4.5:1$	179
C_5	$(CH_3)_3Si(CH=CH)_2CH_2-$ $Si(CH_3)_3$	$n-C_4H_9Li$, THF, -70°	$(CH_3)_3Si(CH=CH)_2CH=C(C_3H_7-i)_2$ (53) ^a	177
		"	(90)	177
	$i-C_3H_7CHO$	"	 (82)	177
	$(CH_3)_2CO$	"	 (83)	177
	$(C_2H_5)_2CO$	"	 (58)	177
	Cyclohexanone	"	 (65)	177
C_{17}		$n-C_4H_9Li$, $t-C_4H_9OK$, THF, $<20^\circ$	$p-(CH_3)_2NC_6H_4$ (79)	298
		"		298
		"	 (58) X = O (61) X = S (44)	298 298

TABLE IV. REACTIONS OF SILANES CONTAINING UNSATURATION WITHOUT ISOLATION OF A β -HYDROXYSILANE (Continued)

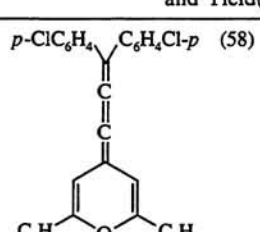
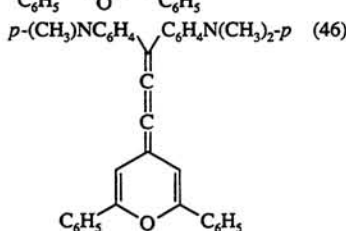
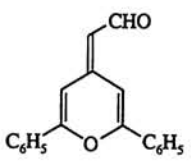
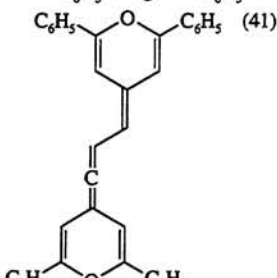
Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, $< -10^\circ$	 (58)	178
		$n\text{-C}_4\text{H}_9\text{Li}$, THF, -10°	 (52)	180
		"	 (56)	180
		"	 (49)	180
		"	 (47)	180
		"	 (38)	180

 C₁₉

134

135

TABLE IV. REACTIONS OF SILANES CONTAINING UNSATURATION WITHOUT ISOLATION OF A β -HYDROXYSILANE (Continued)

Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$(p\text{-ClC}_6\text{H}_4)_2\text{CO}$	"	 <p>$p\text{-ClC}_6\text{H}_4\text{-C}_6\text{H}_4\text{Cl-p}$ (58)</p>	180
	$[p\text{-(CH}_3)_2\text{NC}_6\text{H}_4]_2\text{CO}$	"	 <p>$p\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{N(CH}_3)_2\text{-p}$ (46)</p>	180
		"	 <p>(41)</p>	180

^a All double bonds have the *E* configuration.

^b The yield is determined by GC analysis.

TABLE V. PREPARATION OF UNSATURATED β -HYDROXYSILANES

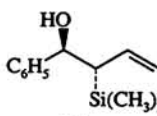
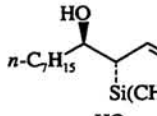
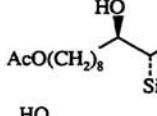
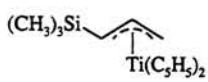
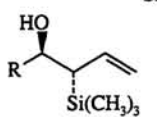
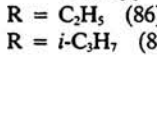
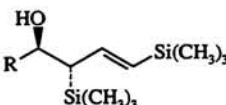
Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
C_2 $(CH_3)_3SiCBr=CH_2$	Cyclopropanone	$t-C_4H_9Li$ (2 eq), THF, -78°	$CH_2=C[Si(CH_3)_3]COH(CH_3)_2$ (60)	170	
	C_6H_5CHO	"	$CH_2=C[Si(CH_3)_3]CHOHC_6H_5$ (64)	134, 170	
	$(C_6H_5)_2CO$	"	$CH_2=C[Si(CH_3)_3]COH(C_6H_5)_2$ (69)	170	
	$(C_6H_5)_3SiCBr=CH_2$	C_6H_5CHO	C_4H_9Li	$CH_2=C[Si(C_6H_5)_3]CHOHC_6H_5$ ($-$) ^a	171
		$C_6H_5CH=CHCHO$	"	$CH_2=C[Si(C_6H_5)_3]CHOHCH=CHC_6H_5$ ($-$) ^a	171
		$n-C_{10}H_{21}CHO$	"	$CH_2=C[Si(C_6H_5)_3]CHOHC_{10}H_{21-n}$ ($-$) ^a	171
	$(C_6H_5)_2CO$	"	$CH_2=C[Si(C_6H_5)_3]COH(C_6H_5)_2$ ($-$) ^a	171	
C_3 $(CH_3)_3SiCH_2CH=CH_2$	C_6H_5CHO	1. $s-C_4H_9Li$ 2. $B(OCH_3)_3$ 3. NH_4Cl , pinacol 4. $N(CH_2CH_2OH)_3$	 (89)	282	
	$n-C_7H_{15}CHO$	"	 (78)	282	
	$AcO(CH_2)_8CHO$	"	 (92)	282	
	$(CH_3)_3Si-CH_2-CH=CH_2$ 	C_2H_5CHO	1. $n-C_4H_9Li$ 2. HCl^b 3. O_2	 (86)	80, 81
		$i-C_3H_7CHO$	"	 (88)	80

TABLE V. PREPARATION OF UNSATURATED β -HYDROXYSILANES (Continued)

Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	<i>t</i> -C ₄ H ₉ CHO	"	R = <i>t</i> -C ₄ H ₉ (98)	80
	Br(CH ₂) ₄ CHO	"	R = Br(CH ₂) ₄ (92)	80
	C ₆ H ₅ CHO	"	R = C ₆ H ₅ (95)	80
(C ₆ H ₅) ₃ SiCH ₂ CH=CH ₂	(C ₆ H ₅) ₂ CO	<i>n</i> -C ₄ H ₉ Li, TMEDA, Et ₂ O	(C ₆ H ₅) ₃ SiCH=CHCH ₂ COH(C ₆ H ₅) ₂ (>95)	173
(CH ₃) ₃ SiCH=CHCH ₂ Si(CH ₃) ₃	<i>n</i> -C ₃ H ₇ CHO	1. <i>n</i> -C ₄ H ₉ Li, THF, -76° 2. MgBr ₂	 R = <i>n</i> -C ₃ H ₇ (74)	28
	"	1. <i>n</i> -C ₄ H ₉ Li, THF, -76° 2. B(OCH ₃) ₃	" (52)	28
	C ₆ H ₅ CHO	"	R = C ₆ H ₅ (50)	28
	"	1. <i>n</i> -C ₄ H ₉ Li, THF, -76° 2. MgBr ₂	" (80)	28
	<i>n</i> -C ₈ H ₁₇ CHO	"	R = <i>n</i> -C ₈ H ₁₇ (80)	28
	"	1. <i>n</i> -C ₄ H ₉ Li, THF, -76° 2. B(OCH ₃) ₃	" (50)	28

^a No specific yield is given, but it is in the range 50–80%.

^b The first step is condensation of the organometallic species with the carbonyl compound.

TABLE VI. ELIMINATIONS FROM UNSATURATED β -HYDROXYSILANES

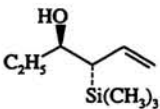
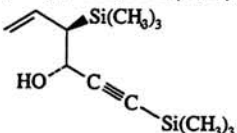
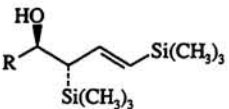
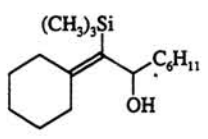
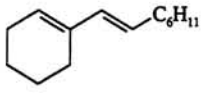
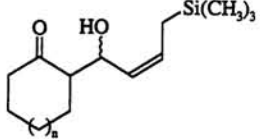
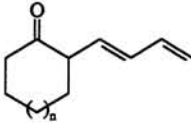
Silane	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 (CH ₃) ₃ SiCH ₂ CHOHCH=CHCH ₃ (CH ₃) ₃ SiCH ₂ COH(CH ₃)CH=CHSi(CH ₃) ₃	CH ₃ SO ₂ Cl, py, 70° NaOAc, AcOH	CH ₂ =CHCH=CHCH ₃ (—) CH ₂ =C(CH ₃)CH=CHSi(CH ₃) ₃ (70)	120 119
C_6  (CH ₃) ₃ SiCH ₂ COH(C ₂ H ₅)CH=CHSi(CH ₃) ₃ 	KH, THF H ₂ SO ₄ , THF NaOAc, AcOH KH, THF	C ₂ H ₅ CH=CHCH=CH ₂ (—) ^a " (—) ^b CH ₂ =C(C ₂ H ₅)CH=CHSi(CH ₃) ₃ (45) CH ₂ =CHCH=CHC≡CSi(CH ₃) ₃ (54) 3Z, 5E:3E, 5E < 5:95	80, 81 80, 81 119 85
	BF ₃ ·OEt ₂	" 3Z, 5E:3E, 5E < 95:5	(85) 85
C_7  R = n-C ₃ H ₇ R = i-C ₃ H ₇ (CH ₃) ₃ SiCH ₂ COH(C ₃ H ₇ -i)CH=CHSi(CH ₃) ₃	KH, THF H ₂ SO ₄ , THF KH, THF H ₂ SO ₄ , THF NaOAc, AcOH	n-C ₃ H ₇ CH=CHCH=CHSi(CH ₃) ₃ (94) 1E, 3E:1E, 3Z:1Z, 3Z = 2:63:35 or <1:90:9° " 1E, 3E:1E, 3Z:1Z, 3Z = 68:3:29 or 92:<1:7° i-C ₃ H ₇ CH=CHCH=CH ₂ (—) ^a " (—) ^b CH ₂ =C(C ₃ H ₇ -i)CH=CHSi(CH ₃) ₃ (65)	28 28 80 80 119

TABLE VI. ELIMINATIONS FROM UNSATURATED β -HYDROXYSILANES (Continued)

Silane	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	KH, THF	$\text{CH}_2\text{CH}=\text{CHCH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ 3Z, 5E:3E, 5E > 95:5	(96) 85
	$\text{BF}_3 \cdot \text{OEt}_2$	" 3Z, 5E:3E, 5E < 5:95	(85) 85
C_8 	KH, THF	$t\text{-C}_4\text{H}_9\text{CH}=\text{CHCH}=\text{CH}_2$ (—) ^a	80
R = $t\text{-C}_4\text{H}_9$	H_2SO_4 , THF	" (—) ^b	80
R = $\text{Br}(\text{CH}_2)_4$	KH, THF	$\text{Br}(\text{CH}_2)_4\text{CH}=\text{CHCH}=\text{CH}_2$ (84) ^a	80
	H_2SO_4 , THF	" (89) ^b	80
	KH, THF	$\text{C}_2\text{H}_5\text{CH}=\text{CHCH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ 3Z, 5E, :3E, 5E = 92:8	(97) 85
	$\text{BF}_3 \cdot \text{OEt}_2$	" 3Z, 5E:3E, 5E = 6:94	(88) 85
C_9 	SnCl_4 , CH_2Cl_2	 (69)	361
C_{10} 	KH, THF	$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{CH}_2$ E:Z = 2:98	(84-88) 80, 282
	H_2SO_4 , THF	" E:Z = 99:1	(85-86) 80, 282
	KH, THF	$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{CHSi}(\text{CH}_3)_3$ 1E, 3E:1E, 3Z:1Z, 3Z = 9:87:4 or 6:81:13 ^c	(90-94) 28
	H_2SO_4 , THF	" 1E, 3E:1E, 3Z:1Z, 3E = 90:6:4 or 84:2:15 ^c	(91-92) 28
$(\text{CH}_3)_3\text{SiCH}_2\text{COH}(\text{C}_6\text{H}_5)\text{CH}=\text{CHSi}(\text{CH}_3)_3$	NaOAc , AcOH	$\text{CH}_2=\text{C}(\text{C}_6\text{H}_5)\text{CH}=\text{CHSi}(\text{CH}_3)_3$ (72)	119
$n\text{-C}_4\text{H}_9$ 	KH, THF	$n\text{-C}_4\text{H}_9\text{CH}=\text{CHCH}=\text{CHC}\equiv\text{CSi}(\text{CH}_3)_3$ 3Z, 5E:3E, 5E = 94:6	(92) 85
C_{11} 	SnCl_4 , CH_2Cl_2	 (80)	361
C_{12} 	KH, THF	$n\text{-C}_8\text{H}_{18}\text{CH}=\text{CHCH}=\text{CH}_2$ 1E, 3E:1E, 3Z:1Z, 3Z = 1:67:32 or <1:90:0 ^c	(91-93) 28
R = $n\text{-C}_8\text{H}_{18}$	H_2SO_4 , THF	" 1E, 3E:1E, 3Z:1Z, 3E = 72:2:26 or 92:<1:7 ^c	(92-95) 28

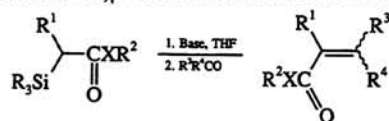
TABLE VI. ELIMINATIONS FROM UNSATURATED β -HYDROXYSILANES (Continued)

Silane	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
R = AcO(CH ₂) ₈	KH, THF	AcO(CH ₂) ₈ CH=CHCH=CH ₂ <i>E:Z</i> = 3:97	(94) 282
	H ₂ SO ₄ , THF	" <i>E:Z</i> = 97:3	(88) 282
C ₆ H ₅ (CH ₂) ₂ CHOHCH=CHCH ₂ Si(CH ₃) ₃	KH, THF	C ₆ H ₅ (CH ₂) ₂ CH=CHCH=CH ₂ (74)	361
C ₁₄ 	1. SOCl ₂ 2. (C ₄ H ₉) ₄ N ⁺ F ⁻	 C ₆ H ₁₁ (72)	155
C ₁₆ n -C ₉ H ₁₉ CH ₂ CH(CH ₃)CHOHCH=CHCH ₂ Si(CH ₃) ₃ 	KH, THF SnCl ₄ , CH ₂ Cl ₂	n -C ₉ H ₁₉ CH ₂ CH(CH ₃)CH=CHCH=CH ₂ (84) 	361
C ₁₇ n = 7		n = 7 (78)	361
n = 8	"	n = 8 (73)	361

^a The *Z* isomer is the major product.

^b The *E* isomer is the major product.

^c The isomer distribution of the products is dependent on the method used for the preparation of the β -hydroxysilane. The first ratio quoted is for the MgBr₂ method of preparation, while the second distribution is for the B(OCH₃)₃ method: see Table V.

TABLE VII. FORMATION OF α,β -UNSATURATED CARBOXYLIC ACID DERIVATIVES








	Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	X	R	R ¹	R ²				
C ₂	N	CH ₃	H	(CH ₃) ₂	CH ₃ CHO	LDA, 0°	CH ₃ CH=CHCON(CH ₃) ₂ (10) ^a	215
					C ₂ H ₅ CHO	"	C ₂ H ₅ CH=CHCON(CH ₃) ₂ (15) ^a	215
					(CH ₃) ₂ CO	"	(CH ₃) ₂ C=CHCON(CH ₃) ₂ (82)	215
						"	 CHCON(CH ₃) ₂ (82)	215
	O	CH ₃	H	H	C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CHCON(CH ₃) ₂ (85) ^a	215
					C ₆ H ₅ CH=CHCHO	"	C ₆ H ₅ CH=CHCH=CHCON(CH ₃) ₂ (89)	215
						LDA (2 eq), -78°	 CO ₂ H (84)	212
					<i>n</i> -C ₅ H ₁₁ CHO	"	<i>n</i> -C ₅ H ₁₁ CH=CHCO ₂ H (90)	212
					"	"	<i>E:Z</i> = 3:2	212
						"	 CO ₂ H (83)	212
O	CH ₃	H	CH ₃	C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CHCO ₂ H (88)	212	
				(CH ₃ O) ₂ CHCOCH ₃	LDA, -78°	(CH ₃ O) ₂ CHCH=C(CH ₃)CO ₂ CH ₃ (55) <i>E:Z</i> = 44:56	49	

TABLE VII. FORMATION OF α,β -UNSATURATED CARBOXYLIC ACID DERIVATIVES (Continued)

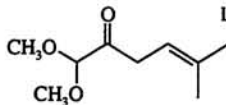
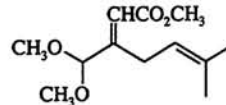
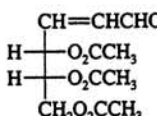
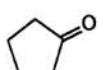
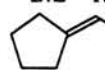
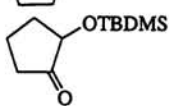
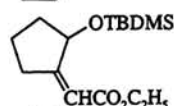
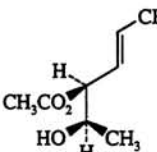
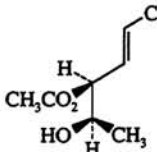
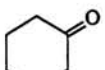
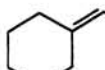
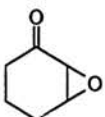
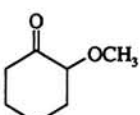
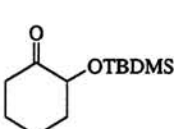
Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	R	R ¹	R ²				
				$n\text{-C}_4\text{H}_9\text{CHO}$	1. LDA, -78° 2. MgBr_2 3. H_2O	$n\text{-C}_4\text{H}_9\text{CH}=\text{CHCO}_2\text{CH}_3$ $E:Z = 98:2$	(74) 41
				"	4. $\text{BF}_3\cdot\text{OEt}_2$, -80° 1. LDA, -78° 2. MgBr_2 3. HMPA	" $E:Z = 15:85$	(75) 41
				$\text{C}_6\text{H}_5\text{CHO}$	1. LDA, -78° 2. MgBr_2 3. H_2O 4. $\text{BF}_3\cdot\text{OEt}_2$	$\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{CH}_3$ $E:Z > 99:1$	(78) 41
				"	1. LDA, -78° 2. MgBr_2 3. HMPA LDA, -78°	" $E:Z = 20:80$	(73) 41
						 (70)	49
				$\text{CH}=\text{CHCHO}$ 	$n\text{-C}_4\text{H}_9\text{Li}$, -78°	$\text{CH}=\text{CHCO}_2\text{CH}_3$ (—)	205
O	CH_3	H	C_2H_5		$\text{LiN}(\text{C}_6\text{H}_{11})_2$, -78°	 (81)	40, 198
					1. LDA, -78° 2. room temp	 (64)	81
					LDA, -78°	 (—)	453
				$n\text{-C}_7\text{H}_{11}\text{CHO}$	1. LDA, -78° 2. MgBr_2 3. HMPA $\text{LiN}(\text{C}_6\text{H}_{11})_2$, -78°	$n\text{-C}_7\text{H}_{11}\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ $E:Z = 29:71$	(65) 41
					$\text{KN}[\text{Si}(\text{CH}_3)_3]_2$, -78°	 (95)	40, 198
						$\text{CHCO}_2\text{C}_2\text{H}_5$ (60)	50
					LDA, -78° ^c	$\text{CHCO}_2\text{C}_2\text{H}_5$ (84)	50
					1. LDA, -78° 2. room temp	$\text{CHCO}_2\text{C}_2\text{H}_5$ (68)	84
				$t\text{-C}_4\text{H}_9\text{COCH}_3$	$\text{LiN}(\text{C}_6\text{H}_{11})_2$, -78°	$t\text{-C}_4\text{H}_9\text{C}(\text{CH}_3)=\text{CHCO}_2\text{C}_2\text{H}_5$ (21) ^b	40
				$\text{C}_6\text{H}_5\text{CHO}$	"	$\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$	(84) 40, 198
				$\text{C}_6\text{H}_5\text{COCH}_3$	"	$\text{C}_6\text{H}_5(\text{CH}_3)\text{C}=\text{CHCO}_2\text{C}_2\text{H}_5$ $E:Z = 2:1$	(63) 40

TABLE VII. FORMATION OF α,β -UNSATURATED CARBOXYLIC ACID DERIVATIVES (Continued)

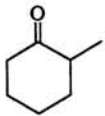
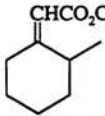
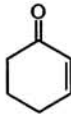
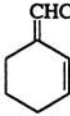
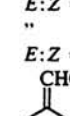
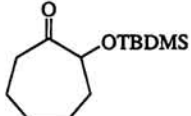
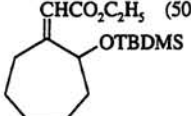
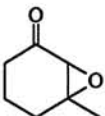
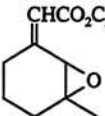
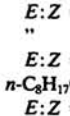
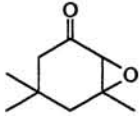
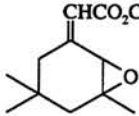
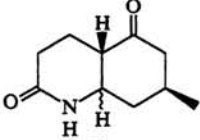
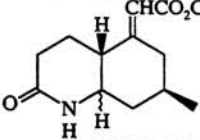
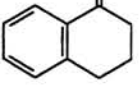
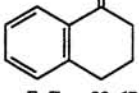
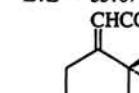
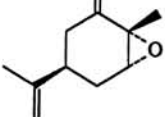
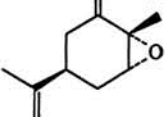
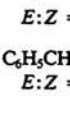
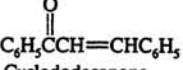
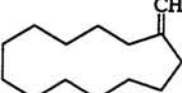
Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	R	R ¹	R ²				
					LDA, -78°C	 (86)	50
					"	 (85)	50
				"	KN[Si(CH ₃) ₃] ₂ , -78°	 E:Z = 55:45	(5) 50
					1. LDA, -78° 2. room temp	 (50)	84
					LDA, -78°C	 (78)	50
				"	KN[Si(CH ₃) ₃] ₂ , -78°	 E:Z = 22:78	(70) 50
				<i>n</i> -C ₈ H ₁₇ CHO	LiN(C ₆ H ₁₁) ₂ , -78°	<i>n</i> -C ₈ H ₁₇ CH=CHCO ₂ C ₂ H ₅ E:Z = 1:1	(81) 40, 198
					LDA, -78°C	 (87)	50
					<i>n</i> -C ₄ H ₉ Li, -60°	 (—)	206
					LDA, -78°C	 (82)	50
				"	"	 E:Z = 33:67	(90) 50
					"	 (90)	50
				"	"	 E:Z = 10:90	
				 C ₆ H ₅ CCH=CHC ₆ H ₅	LiN(C ₆ H ₁₁) ₂ , -78°	C ₆ H ₅ CH=CHC(C ₆ H ₅)=CHCO ₂ H ₅ (86) E:Z = 7:3	40, 198
				Cyclododecanone	"	 (94)	40, 198

TABLE VII. FORMATION OF α,β -UNSATURATED CARBOXYLIC ACID DERIVATIVES (Continued)

Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	R	R ¹	R ²				
					"		(82) 40
				CH_3S SCH_3 C_6H_{11} CHO	LDA, -78°	CH_3S SCH_3 C_6H_{11} $\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$	(92) ^b 48
				$\text{CH}_2=\text{CH}(\text{CH}_2)_7$ $\text{C}(\text{SCH}_3)_2\text{CHO}$	"	$\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{C}(\text{SCH}_3)\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$	(92) ^b 48
				$\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9-t$	"	$\text{OSi}(\text{CH}_3)_2\text{C}_4\text{H}_9-t$	(76) ^b 48
				$\text{CH}_3\text{CH}(\text{CH}_2)_7\text{C}(\text{SCH}_3)_2\text{CHO}$ $p\text{-CH}_3\text{OC}_6\text{H}_4(\text{CH}_2)_2\text{C}(\text{SCH}_3)_2\text{CHO}$	"	$\text{CH}_3\text{CH}(\text{CH}_2)_7\text{C}(\text{SCH}_3)_2\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ $p\text{-CH}_3\text{OC}_6\text{H}_4(\text{CH}_2)_2\text{C}(\text{SCH}_3)_2\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$	(90) ^b 48
				OCH_3	"	OCH_3	(87) ^b 48
					LDA, -35°		(-) 200
					LDA, -35°		(-) 200
					LiN(C ₆ H ₁₁) ₂ , -78°		(80) 199
					1. LDA, -78° 2. (NH ₄) ₂ SO ₄ , H ₂ O		(47) 461
O	CH ₃	H	<i>i</i> -C ₃ H ₇	<i>i</i> -C ₃ H ₇ CHO	1. LDA, -78° 2. MgBr ₂ 3. HMPA LDA, -78°	<i>i</i> -C ₃ H ₇ CH=CHCO ₂ C ₃ H ₇ - <i>i</i>	(75) 41
					LDA, -78°		(73) 49
					"		(76) 49
O	CH ₃	H	<i>t</i> -C ₄ H ₉	CH ₃ CHO	"	CH ₃ CH=CHCO ₂ C ₄ H ₉ - <i>t</i>	(93) ^d 201
				(CH ₃ O) ₂ CHCHO	"	(CH ₃ O) ₂ CHCH=CHCO ₂ C ₄ H ₉ - <i>t</i>	(63) 49
				(CH ₃) ₂ CO	"	(CH ₃) ₂ C=CHCO ₂ C ₄ H ₉ - <i>t</i>	(53) 201
				<i>i</i> -C ₃ H ₇ CHO	"	<i>i</i> -C ₃ H ₇ CH=CHCO ₂ C ₄ H ₉ - <i>t</i>	(66) ^d 201
				CH ₃ CH=CHCHO	"	CH ₃ CH=CHCH=CHCO ₂ C ₄ H ₉ - <i>t</i>	(78) ^a 201

TABLE VII. FORMATION OF α,β -UNSATURATED CARBOXYLIC ACID DERIVATIVES (Continued)



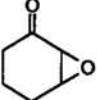
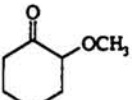
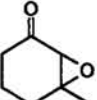
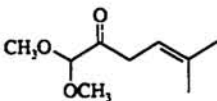
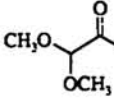
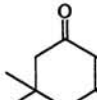
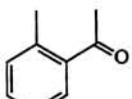
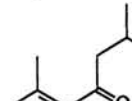
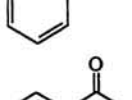
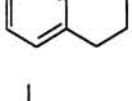
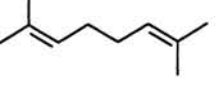
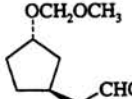
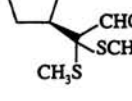
Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	R	R ¹	R ²				
				$(\text{CH}_3\text{O})_2\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$	"	$(\text{CH}_3\text{O})_2\text{CHC}(\text{C}_4\text{H}_9\text{-}t)=\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$ $E:Z = 16:84$	49
					"	 (90)	201
					"	$\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$ (60)	50
					"	$E:Z = 22:78$ $\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$ (63)	50
				$\text{C}_6\text{H}_5\text{CHO}$	"	$E:Z = 13:87$ $\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$ (75) ^d	201
					"	$\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$ (77)	50
					"	$E:Z = 17:83$ $\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$ (77)	49
					"	$E:Z = 12:88$	
				$\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$	"	$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$ (58) ^d	201
					"	$\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$ (87)	50
					1. LDA, -78° 2. CF ₃ CO ₂ H, H ₂ O	$E:Z = 10:90$ (60) ^d	202
					"	(52) ^d	202
					LDA, -78°	$\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$ (56)	50
					"	$E:Z = 18:82$ $t\text{-C}_4\text{H}_9\text{O}_2\text{CCH}$ (81)	41
					"	$E:Z = 2:98$ $\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$ (85) ^d	48
					"	$\text{CH}=\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$	
					"	$\text{CH}=\text{CHCO}_2\text{C}_4\text{H}_9\text{-}t$	

TABLE VII. FORMATION OF α,β -UNSATURATED CARBOXYLIC ACID DERIVATIVES (Continued)

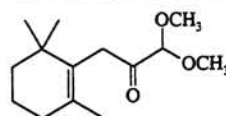
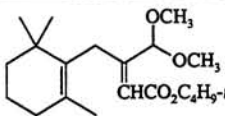
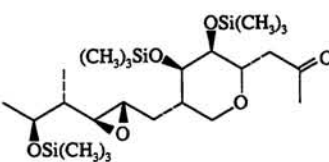
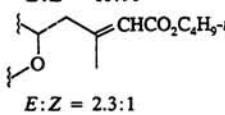
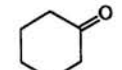
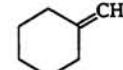
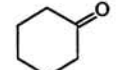
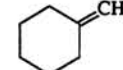
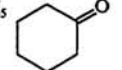
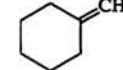
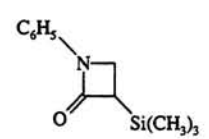
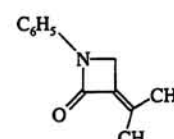
	Silane			Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	X	R	R ¹				
					"	 (71)	49
					"	 (46)	45
	O	C ₆ H ₅ - (CH ₃) ₂	H	C ₂ H ₅ <i>i</i> -C ₃ H ₇ CHO	"	<i>i</i> -C ₃ H ₇ CH=CHCO ₂ H ₅ <i>E:Z</i> = 86:14	(-) ^r 42
				"	1. LDA, -78° 2. 0°	" <i>E:Z</i> = 30:70	(-) ^r 42
				"	LDA, TMEDA (2 eq), -78°	"	(-) ^r 42
				"	LDA, HMPA (2 eq), -78°	<i>E:Z</i> = 55:45	(-) ^r 42
				"	LDA, 12-crown-4, -78°	<i>E:Z</i> = 36:44	(-) ^r 42
				"	"	<i>E:Z</i> = 30:70	(-) ^r 42
	O	C ₆ H ₅ - (CH ₃) ₂	H	<i>i</i> -C ₃ H ₇	LDA, -78°	<i>i</i> -C ₃ H ₇ CH=CHCO ₂ C ₃ H ₇ - <i>i</i> <i>E:Z</i> = 40:60	(-) ^r 42
				"	LDA, HMPA (2 eq), -78°	" <i>E:Z</i> = 16:50 Aldehyde trimer (34)	(-) ^r + 42
	O	C ₆ H ₅ - (CH ₃) ₂	H	<i>t</i> -C ₄ H ₉	LDA, -78°	<i>i</i> -C ₃ H ₇ CH=CHCO ₂ C ₄ H ₉ - <i>t</i> <i>E:Z</i> = 40:60	(-) ^r 42
	O	C ₆ H ₅ - (CH ₃) ₂	H	(-)-menthyl C ₆ H ₅ CH=CHCHO	"	<i>i</i> -C ₃ H ₇ CH=CHCO ₂ (-)-menthyl <i>E:Z</i> = 86:14	(-) ^r 42
				"	"	C ₆ H ₅ CH=CHCH=CHCO ₂ - (-)-menthyl <i>E:Z</i> = 57:43	(-) ^r 42
	S	CH ₃	H	<i>i</i> -C ₃ H ₇ <i>i</i> -C ₃ H ₇ CHO	"	<i>i</i> -C ₃ H ₇ CH=CHCOSC ₃ H ₇ - <i>i</i> <i>E:Z</i> > 95:5	(51) 213
					"	 (62)	213
				C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CHCOSC ₃ H ₇ - <i>i</i> <i>E:Z</i> > 95:5	(65) 213
	S	CH ₃	H	<i>t</i> -C ₄ H ₉ 	"	 (77)	213
				C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CHCOSC ₄ H ₉ - <i>t</i> <i>E:Z</i> > 95:5	(73) 213
				C ₆ H ₅ COCH ₃	"	C ₆ H ₅ C(CH ₃)=CHCOSC ₄ H ₉ - <i>t</i> <i>E:Z</i> > 95:5	(52) 213
	S	CH ₃	H	CH ₂ C ₆ H ₅ 	"	 (49)	213
				C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CHCOSC ₂ C ₆ H ₅ <i>E:Z</i> > 95:5	(54) 213
	C ₃			(CH ₃) ₂ CO	LDA	 (93)	218

TABLE VII. FORMATION OF α,β -UNSATURATED CARBOXYLIC ACID DERIVATIVES (Continued)


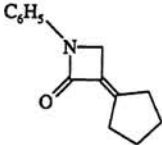

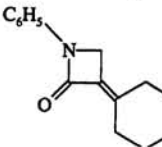
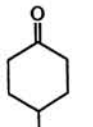
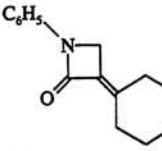
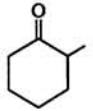
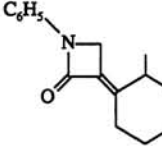
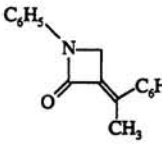









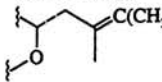
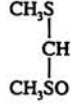
X	Silane			Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	R	R ¹	R ²				
					"	 (77)	218
					"	 (86)	218
					"	 (87)	218
					"	 (36)	218
				C ₆ H ₅ COCH ₃	"	 (43) ^f	218
O	CH ₃	CH ₃	C ₂ H ₅	CH ₂ =CHCHO	LDA, -78°	CH ₂ =CHCH=C(CH ₃)CO ₂ H ₅ (65)	209
				(CH ₃) ₂ CO	"	<i>E:Z</i> = 23:77	
				<i>n</i> -C ₃ H ₇ CHO	"	(CH ₃) ₂ C=C(CH ₃)CO ₂ C ₂ H ₅ (84)	209
				<i>i</i> -C ₃ H ₇ CHO	"	<i>n</i> -C ₃ H ₇ CH=C(CH ₃)CO ₂ C ₂ H ₅ (57)	209
					"	<i>E:Z</i> = 25:75	
				<i>n</i> -C ₆ H ₁₃ CHO	"	<i>i</i> -C ₃ H ₇ CH=C(CH ₃)CO ₂ C ₂ H ₅ (60)	209
					"	<i>E:Z</i> = 10:90	
					"	C(CH ₃)CO ₂ C ₂ H ₅ (77)	209
					"	<i>n</i> -C ₆ H ₁₃ CH=C(CH ₃)CO ₂ C ₂ H ₅ (69)	209
					"	<i>E:Z</i> = 25:75	
					"	C(CH ₃)CO ₂ C ₂ H ₅ (77)	
					"	<i>E:Z</i> = 1:3	
					"	"	
					1. LDA, -78° 2. MgBr ₂ LDA, -78°	<i>E:Z</i> = 37:15 " (43)	(52) 45
O	C ₆ H ₅ (CH ₃) ₂	CH ₃	C ₂ H ₅	"	"	<i>E:Z</i> = 1:1.6	45
O	CH ₃	CH ₃	<i>i</i> -C ₄ H ₉	"	"	 (70)	45
				"	"	all TMS now OH	
				"	"	<i>E:Z</i> = 1:7.2	
O	CH ₃		CH ₃	C ₂ H ₅ CHO	CH ₃ SCHLiSOCH ₃ , CH ₂ =C[Si(CH ₃) ₃], -78°	CH ₃ SCH(SOCH ₃)CH ₂ C(CO ₂ CH ₃)=CH- C ₂ H ₅ (72)	204
				C ₆ H ₅ CHO	"	<i>E:Z</i> = 1:1	
				"	"	CH ₃ SCH(SOCH ₃)CH ₂ C(CO ₂ CH ₃)=CH- C ₆ H ₅ (90)	204
				"	"	<i>E:Z</i> = 100:0	

TABLE VII. FORMATION OF α,β -UNSATURATED CARBOXYLIC ACID DERIVATIVES (Continued)

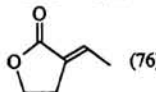
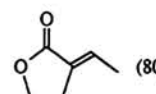
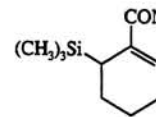
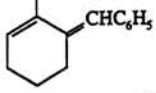
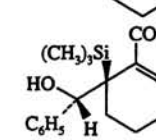
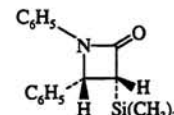
	Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	X	R	R ¹	R ²				
					$C_6H_5CH=CHCHO$	"	$CH_3S(CH_2SO)CHCH_2C(CO_2CH_3)=CH-CH=CHC_6H_5$ (71) $E:Z = 100:0$	204
C ₄	O	C_6H_5- (CH_3) ₂	C_2H_5	C_2H_5	$i-C_3H_7CHO$	LDA, -78°	$i-C_3H_7CH=C(C_2H_5)CO_2H_5$ $E:Z = 18:82$	(55) 204
					C_6H_5CHO	"	$C_6H_5CH=C(C_2H_5)CO_2H_5$ $E:Z = 20:80$	(73) 204
	O	CH_3	$-(CH_2)_2-$		CH_3CHO	$(C_6H_5)_3CLi$, -78°	 (76)	212
C ₅	O	CH_3	$-CH_2CH(CH_3)-$		"	"	 (80)	212
C ₆	O	CH_3	$CH_2=CH$ $CH_2=C$ CH_2		$t-C_4H_9CHO$	$CH_2=CHC(Li)=CH_2$, $CH_2=C[Si(CH_3)_3]$ CO_2CH_3 , -78°	$CH_2=CH$ $CH_2=CCH_2C(CO_2CH_3)=CHC_4H_9-t$ $E:Z = 0:100$	(47) 204
					C_6H_5CHO	"	$CH_2=CH$ $CH_2=CCH_2C(CO_2CH_3)=CHC_6H_5$ $E:Z = 2:1$	(74) 204
					$C_6H_5CH=CHCHO$	"	$CH_2=CH$ CO_2CH_3 $CH_2=CCH_2C=CHCH=CHC_6H_5$ $E:Z = 1:3$	(45) 204
C ₇					C_6H_5CHO	$s-C_4H_9Li$, TMEDA, -78°	$CON(C_2H_5)_2$ (44) +  (17) +  (-)	220, 221
C ₈					CH_3CHO	LDA, -78°	C_6H_5 C_6H_5 $CHCH_3$ $E:Z = 1:1$	(60) 219
					"	"	" $E:Z = 6:4$	(33) 219
					$p-O_2NC_6H_4CHO$	"	C_6H_5 C_6H_5 $CHC_6H_4NO_2-p$ $E:Z = 1:2$	(22) 219

TABLE VII. FORMATION OF α,β -UNSATURATED CARBOXYLIC ACID DERIVATIVES (Continued)

Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
X	R	R ¹	R ²					
				"	"	" <i>E:Z</i> = 1:2	(68) 219	
				<i>o</i> -ClC ₆ H ₄ CHO	"	 <i>E:Z</i> = 0:100	(29) 219	
				"	"	"	<i>E:Z</i> = 0:100	(17) 219
				<i>p</i> -(CH ₃) ₂ NC ₆ H ₄ CHO	"	 <i>E:Z</i> = 1:1	(28) 219	
				"	"	"	<i>E:Z</i> = 1:1	(64) 219
O	CH ₃	C ₆ H ₅ (CH ₂) ₂	CH ₃	(CH ₃) ₂ CO	C ₆ H ₅ MgBr, CuCl, Et ₂ O, -15°, CH ₂ =C[Si-(CH ₃) ₃]- CO ₂ CH ₃	C ₆ H ₅ CH ₂ C(CO ₂ CH ₃)=C(CH ₃) ₂	(73) 204	
				CH ₃ CH=CHCHO	"	C ₆ H ₅ CH ₂ C(CO ₂ CH ₃)=CHCH=CHCH ₃	<i>E:Z</i> = 3:7 (59) 204	
				<i>t</i> -C ₄ H ₉ CHO	"	C ₆ H ₅ CH ₂ C(CO ₂ CH ₃)=CHCO ₂ C ₄ H ₉ - <i>t</i>	<i>E:Z</i> = 3:2 (54) 204	
					"		(40) 204	
				C ₆ H ₅ CHO	"	C ₆ H ₅ CH ₂ C(CO ₂ CH ₃)=CHC ₆ H ₅	(80) 204 <i>E:Z</i> = 1:4	
C ₁₀	O	CH ₃	-CH ₂ CH(C ₆ H ₁₃ - <i>n</i>)-	CH ₃ CHO	(C ₆ H ₅) ₃ CLi, -78°		(60) 212	
O	C ₆ H ₅ - (CH ₃) ₂	<i>n</i> -C ₈ H ₁₇	C ₂ H ₅	<i>n</i> -C ₃ H ₇ CHO	LDA, -78°	<i>n</i> -C ₃ H ₇ CH=C(C ₆ H ₁₇ - <i>n</i>)CO ₂ C ₂ H ₅	(-) 209 <i>E:Z</i> = 33:67	
				"	1. LDA, -78° 2. H ₂ O 6. BF ₃ ·OEt ₂	"	<i>E:Z</i> = 12:88	(-) 209
				<i>n</i> -C ₆ H ₁₃ CHO	LDA, -78°	<i>n</i> -C ₆ H ₁₃ CH=C(C ₆ H ₁₇ - <i>n</i>)CO ₂ C ₂ H ₅	(62) 209 <i>E:Z</i> = 29:71	

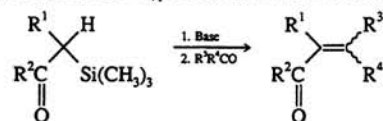
^a The yield is determined by GC analysis.

^b No *Z* isomer is detected.

^c These conditions are inferred from the text.

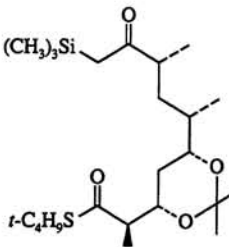
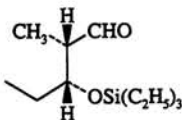
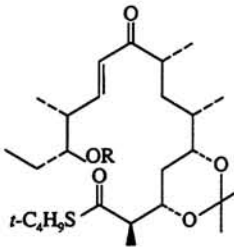
^d The isomer ratio is not stated.

^e No specific yield is given but it is in the 60–80% range.

TABLE VIII. FORMATION OF α,β -UNSATURATED CARBONYL COMPOUNDS

	Silane		Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.				
	R ¹	R ²								
160	C ₂	H	Fe(CO)[P(C ₆ H ₅) ₃] ₂ (C ₃ H ₅)	CH ₂ O	<i>n</i> -C ₄ H ₉ Li, -78°	[(C ₆ H ₅) ₃ P](CO)(C ₃ H ₅)FeCO-CH=CHR	51			
				CH ₃ CHO	"	R = H (30)	51			
				C ₂ H ₅ CHO	"	R = CH ₃ (88) <i>E:Z</i> = 2:1	51			
				CH ₂ =CHCHO	"	R = C ₂ H ₅ (77) <i>E:Z</i> = 2:1	51			
				<i>n</i> -C ₄ H ₉ Li	"	R = CH=CH ₂ (68) <i>E:Z</i> = 3:2	51			
				<i>t</i> -C ₄ H ₉ Li	"	R = C ₄ H ₉ - <i>n</i> (88) <i>E:Z</i> = 3:2	51			
				Furfural	"	R = C ₄ H ₉ - <i>t</i> (63) <i>E:Z</i> = 100:0	51			
				C ₆ H ₅ CHO	"	R = 2-Furyl (78) <i>E:Z</i> = 3:2	51			
					"	R = C ₆ H ₅ (80) <i>E:Z</i> = 3:2	51			
				161	C ₃	CH ₃	Si(CH ₃) ₃	C ₂ H ₅ CHO	1. LDA, 0° 2. -78°	C ₂ H ₅ CH=C(CH ₃)COSi(CH ₃) ₃ (82) ^a
<i>i</i> -C ₃ H ₇ CHO	"	<i>i</i> -C ₃ H ₇ CH=C(CH ₃)COSi(CH ₃) ₃ (90) ^a	44							
(<i>E</i>)-CH ₃ CH=CHCHO	"	(<i>E</i>)-CH ₃ CH=CHCH=C(CH ₃)COSi(CH ₃) ₃ (91) ^a	44							
<i>n</i> -C ₄ H ₉ CHO	"	<i>n</i> -C ₄ H ₉ CH=C(CH ₃)COSi(CH ₃) ₃ (78) ^a	44							
<i>s</i> -C ₄ H ₉ CHO	"	<i>s</i> -C ₄ H ₉ CH=C(CH ₃)COSi(CH ₃) ₃ (85) ^a	44							
<i>t</i> -C ₄ H ₉ CHO	LDA, 0°	<i>t</i> -C ₄ H ₉ CH=C(CH ₃)COSi(CH ₃) ₃ (72) ^a	44							
<i>n</i> -C ₄ H ₉ C≡CCHO	1. LDA, 0° 2. -78°	<i>n</i> -C ₄ H ₉ C≡CCH=C(CH ₃)COSi(CH ₃) ₃ (78) ^a	44							
C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(CH ₃)COSi(CH ₃) ₃ (84) ^a	44							
C ₅	H	C ₂ H ₅ Si(CH ₃) ₃	<i>i</i> -C ₃ H ₇ CH ₂ CHO					(CH ₃) ₃ SiCHLiC ₃ H ₁₁ - <i>n</i> , -78°	C ₂ H ₅ COCH=CHCH ₂ C ₃ H ₇ - <i>i</i> (75) ^b	61
			<i>n</i> -C ₄ H ₉ CHO					1. LDA, 0° 2. -78°	<i>n</i> -C ₄ H ₉ CH=C(C ₄ H ₉ - <i>n</i>)COSi(CH ₃) ₃ (80) ^a	44
C ₇	H	<i>n</i> -C ₅ H ₁₁	<i>t</i> -C ₄ H ₉ CHO	(CH ₃) ₃ SiCHLiC ₃ H ₁₁ - <i>n</i> , -78°	<i>n</i> -C ₅ H ₁₁ COCH=C(C ₅ H ₁₁ - <i>n</i>)CO-Si(CH ₃) ₃ (75) ^b	61				
			(<i>E</i>)- <i>n</i> -C ₃ H ₇ CH=CHCHO	"	(<i>E</i>)- <i>n</i> -C ₃ H ₇ CH=CHCH=C(C ₅ H ₁₁ - <i>n</i>)COSi(CH ₃) ₃ (81) ^b	61				
			C ₆ H ₁₁ CHO	"	C ₆ H ₁₁ CH=C(C ₅ H ₁₁ - <i>n</i>)COSi(CH ₃) ₃ (88) ^b	61				
			C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(C ₅ H ₁₁ - <i>n</i>)COSi(CH ₃) ₃ (91) ^b	61				
			<i>n</i> -C ₈ H ₁₇ CHO	"	<i>n</i> -C ₈ H ₁₇ CH=C(C ₅ H ₁₁ - <i>n</i>)COSi(CH ₃) ₃ (82) ^b	61				
C ₉	C ₆ H ₅ CH ₂	Si(CH ₃) ₃	CH ₃ CHO	1. LDA, 0° 2. -78°	CH ₃ CH=C(CH ₂ C ₆ H ₅)COSi(CH ₃) ₃ (84) ^a	44				

TABLE VIII. FORMATION OF α,β -UNSATURATED CARBONYL COMPOUNDS (*Continued*)

Silane		Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
R ¹	R ²				
C ₁₀					
		LiN[Si(CH ₃) ₃] ₂ , -78°		(95)	188
R = Si(C ₂ H ₅) ₃					

^a No *Z* isomer is detected.

^b The *E:Z* isomer ratio is not quoted.

TABLE IX. NITROGEN-CONTAINING α -SILYL CARBANIONS

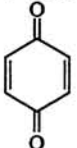
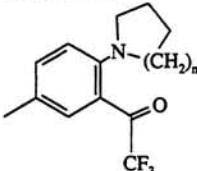
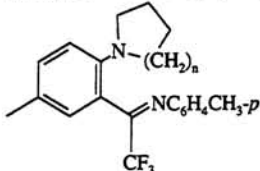
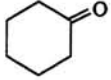
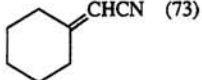
Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_0 [[CH ₃] ₃ Si] ₂ NH	C ₆ H ₅ CHO	NaH, C ₆ H ₆ , 70°	(CH ₃) ₃ SiN=CHC ₆ H ₅ (61)	226
	(C ₆ H ₅) ₂ CO	"	(CH ₃) ₃ SiN=C(C ₆ H ₅) ₂ (84)	226
		"	NSi(CH ₃) ₃ (20)	226
p -CH ₃ C ₆ H ₄ NHSi(CH ₃) ₃	<i>t</i> -C ₄ H ₉ NCO	<i>n</i> -C ₄ H ₉ Li, C ₆ H ₁₂	(CH ₃) ₃ SiN=C=NC ₄ H ₉ - <i>t</i> (56)	356
		<i>n</i> -C ₄ H ₉ Li, THF, -78°		229
	$n = 1$		$n = 1$ (74)	
	$n = 2$		$n = 2$ (69)	
C_1 (CH ₃) ₃ SiCH ₂ CN		LDA, Et ₂ O, -78°	 (73)	224
	C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CHCN	(77) 224
	C ₆ H ₅ CH=CHCHO	"	C ₆ H ₅ CH=CHCH=CHCN (95) ^a	224

TABLE IX. NITROGEN-CONTAINING α -SILYL CARBANIONS (Continued)

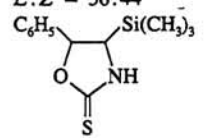
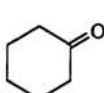
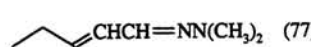
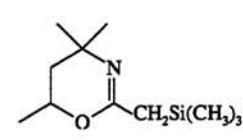
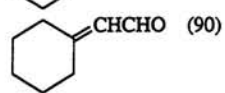
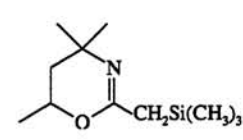
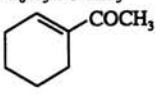
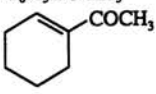
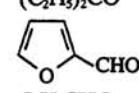
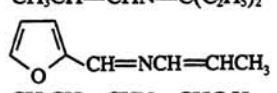
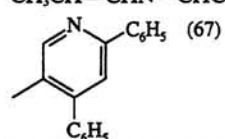
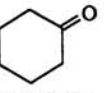
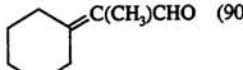
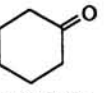
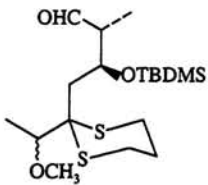
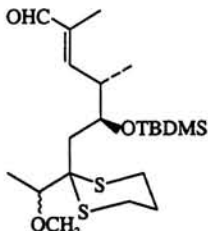
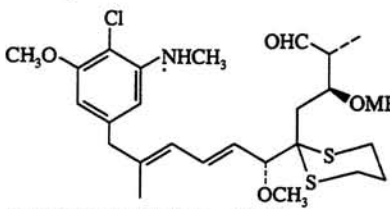
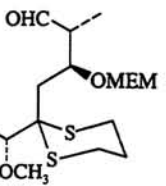
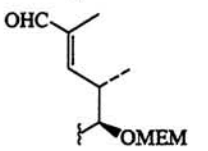
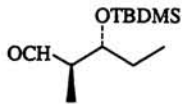
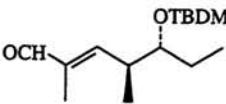


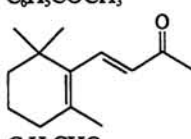
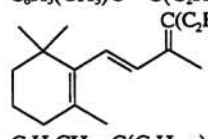
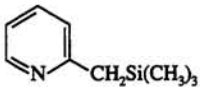
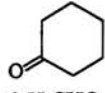
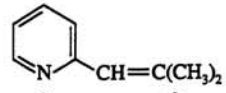
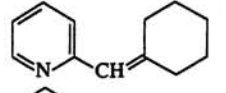
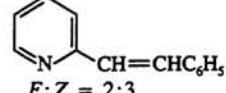
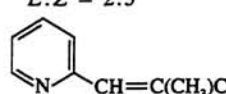
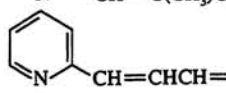
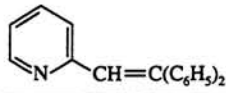
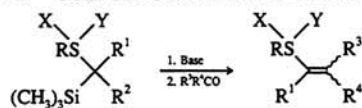
Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
$[(CH_3)_3Si]_2CHNCS$	C_6H_5CHO	1. $(C_4H_9)_4N^+F^-$, THF 2. H_2O	$C_6H_5CH=CHNCS$ (31) + $E:Z = 56:44$  (6)	224	
C_2	$(CH_3)_3SiCH_2CH=NN(CH_3)_2$	$CH_3CH=CHCHO$	LDA, THF, -78°	$CH_3CH=CHCH=CHCH=NN(CH_3)_2$ (80)	236
		$n-C_3H_7CHO$	"	$n-C_3H_7CH=CHCH=NN(CH_3)_2$ (93)	236
		"	1. LDA, THF, -78° 2. H_2O , $(CO_2H)_2$ LDA, THF, -78°	$n-C_3H_7CH=CHCHO$ (94)	231
		"	"	 $CHCH=NN(CH_3)_2$ (77)	236
		C_6H_5CHO	1. LDA, THF, -78°	 $CHCHO$ (90)	231
		$C_2H_5COCH_3$	2. H_2O , $(CO_2H)_2$ LDA, THF, -78° $n-C_4H_9Li$, THF, -78°	$C_6H_5CH=CHCH=NN(CH_3)_2$ (95)	236
		$C_2H_5COCH_3$	"	$CH=C(CH_3)R$	222
		$i-C_3H_7CHO$	"	$R = C_2H_5$ (80-95) ^b $E:Z = 96:4^c$	
		$C_6H_5COCH_3$	"	$R = i-C_3H_7$ (80-95) ^b $E:Z = 85:15^c$	222
		$COCH_3$	"	$R = C_6H_5$ (80-95) ^b $E:Z = 95:5^c$	222
		"	(80-95) ^b	222	
"		"	$E:Z = 95:5^c$		
C_3	$[(CH_3)_3Si]_2NCH=CHCH_3$	$i-C_3H_7CHO$	$(C_4H_9)_4N^+F^-$, THF	$CH_3CH=CHN=CHC_2H_5-i$ (50) ^a	230
		$(C_2H_5)_2CO$	CsF, DMF, 80°	$CH_3CH=CHN=C(C_2H_5)_2$ (30)	230
			$(C_4H_9)_4N^+F^-$, THF	 $CH=NCH=CHCH_3$ (23) ^a	230
	C_6H_5CHO	C_6H_5CHO	CsF, DMF, 80°	$CH_3CH=CHN=CHC_6H_5$ (80) ^a	230
		$C_6H_5CH=CHCHO$	$(C_4H_9)_4N^+F^-$, THF	$CH_3CH=CHN=CHCH=CHC_6H_5$ (29) ^a	230
		"	CsF, DMF, 80°	 (67)	230
	$(CH_3)_3SiCH(CH_3)CH=NN(CH_3)_2$	$(C_6H_5)_2CO$	CsF, DMF, 80°	$CH_3CH=CHN=C(C_6H_5)_2$ (80)	230
		$i-C_3H_7CHO$	1. LDA, THF, 0° 2. H_2O , $(CO_2H)_2$	$E:Z = 62:38$ $i-C_3H_7CH=C(CH_3)CHO$ (88)	231
		"	"	$i-C_3H_7CH=C(CH_3)CHO$ (88)	231
		C_6H_5CHO	"	 $C(CH_3)CHO$ (90)	231
	"	"	$C_6H_5CH=C(CH_3)CHO$ (90)	231	
	C_6H_5CHO	"	$E:Z = 1:1$		

TABLE IX. NITROGEN-CONTAINING α -SILYL CARBANIONS (Continued)

Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
$(\text{CH}_3)_3\text{SiCH}(\text{CH}_3)\text{CH}=\text{NC}_4\text{H}_9\text{-}t$		1. $s\text{-C}_4\text{H}_9\text{Li}$, THF, -78° 2. NaOAc, AcOH, H_2O 3. SiO_2 , CH_2Cl_2	 (80)	233
		1. LDA, THF, -110° 2. -78° 3. SiO_2 4. $\text{Py}\cdot\text{HCl}$, CH_2Cl_2	 (82)	234
$(\text{C}_2\text{H}_5)_3\text{SiCH}(\text{CH}_3)\text{CH}=\text{NC}_4\text{H}_9\text{-}t$		$s\text{-C}_4\text{H}_9\text{Li}$, THF	 (77)	235
$\text{C}_2\text{H}_5\text{CH}[\text{SiC}_6\text{H}_5(\text{CH}_3)_2]\text{CN}$ $\text{C}_2\text{H}_5\text{CH}[\text{SiC}_6\text{H}_5(\text{CH}_3)_2]\text{CN}$	$\text{C}_6\text{H}_5\text{CHO}$ $\text{CH}_3\text{CH}=\text{CHCHO}$ $(\text{CH}_3)_2\text{CO}$ $\text{C}_2\text{H}_5\text{COCH}_3$  $\text{C}_6\text{H}_5\text{CHO}$	LDA, THF, -78° " " " "	$\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_2\text{H}_5)\text{CN}$ (98) $\text{CH}_3\text{CH}=\text{CHCH}=\text{C}(\text{C}_2\text{H}_5)\text{CN}$ (91) ^d $(\text{CH}_3)_2\text{C}=\text{C}(\text{C}_2\text{H}_5)\text{CN}$ (92) ^d $\text{C}_2\text{H}_5\text{C}(\text{CH}_3)=\text{C}(\text{C}_2\text{H}_5)\text{CN}$ (95) ^d  $\text{C}(\text{C}_2\text{H}_5)\text{CN}$ (96) ^d $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_2\text{H}_5)\text{CN}$ (98) ^d	223 223 223 223 223
$n\text{-C}_3\text{H}_7\text{CH}[\text{SiC}_6\text{H}_5(\text{CH}_3)_2]\text{CN}$ $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{CH}[\text{SiC}_6\text{H}_5(\text{CH}_3)_2]\text{CN}$	$\text{C}_6\text{H}_5\text{COCH}_3$  $\text{C}_6\text{H}_5\text{CHO}$ "	" " " "	$\text{C}_6\text{H}_5(\text{CH}_3)\text{C}=\text{C}(\text{C}_2\text{H}_5)\text{CN}$ (98) ^d $\text{C}(\text{C}_2\text{H}_5)\text{CN}$ (93) ^d  $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_2\text{H}_7\text{-}n)\text{CN}$ (97) ^d $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{CH}_2\text{C}_6\text{H}_5)\text{CN}$ (92)	223 223
	$(\text{CH}_3)_2\text{CO}$  $\text{C}_6\text{H}_5\text{CHO}$	LDA, THF, -70° " "	 (71) ^d  (58)  (19) $\text{CH}=\text{CHC}_6\text{H}_5$ $E:Z = 2:3$ (67)  (53)  (70) 	96 96 96 96 96

^a The *E:Z* isomer ratio is not given.^b The exact yield is not given.^c The isomer ratio is determined by GLC analysis.^d The yield is from GLC analysis.

TABLE X. SULFUR-CONTAINING α -CARBANIONS










Silane					Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
X	Y	R	R ¹	R ^{2a}					
C ₁	—	—	CH ₃	H	H	C ₆ H ₅ CHO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	C ₆ H ₅ CH=CHSCH ₃ <i>E:Z</i> = 1:1 (64)	3
						(C ₆ H ₅) ₂ CO	"	(C ₆ H ₅) ₂ C=CHSCH ₃ (56)	3
						C ₆ H ₅ CON(CH ₂) ₃	"	C ₆ H ₅ [N(CH ₂) ₃]C=CHSCH ₃ <i>E:Z</i> = 87:13 (72)	243, 244
	—	—	C ₆ H ₅	H	H	CH ₂ O	"	CH ₂ =CHSC ₆ H ₅ (65)	157
						CH ₃ CHO	<i>n</i> -C ₄ H ₉ Li, TMEDA, C ₆ H ₁₄ , 0° <i>n</i> -C ₄ H ₉ Li, THF, 0°	" (63) CH ₃ CH=CHSC ₆ H ₅ (58)	157 157
						(CH ₃) ₂ CO	"	(CH ₃) ₂ C=CHSC ₆ H ₅ (50, 62)	157, 239
						CH ₂ =CHCOCH ₃	"	CH ₂ =CHC(CH ₃)=CHSC ₆ H ₅ (71)	242
						<i>n</i> -C ₄ H ₉ CHO	"	<i>n</i> -C ₄ H ₉ CH=CHSC ₆ H ₅ <i>E:Z</i> ~ 1:1 (67)	157
						CH ₃ CH=CHCOCH ₃	"	CH ₃ CH=CHC(CH ₃)=CHSC ₆ H ₅ (95)	242
						<i>i</i> -C ₃ H ₇ COCH ₃	"	<i>i</i> -C ₃ H ₇ C(CH ₃)=CHSC ₆ H ₅ (68)	157
						(C ₂ H ₅) ₂ CO	"	(C ₂ H ₅) ₂ C=CHSC ₆ H ₅ (71)	157
							"	 (60)	157
						(CH ₃) ₂ C=CHCOCH ₃	"	(CH ₃) ₂ C=C(CH ₃)=CHSC ₆ H ₅ (85)	242
						<i>n</i> -C ₃ H ₁₁ CHO	"	<i>n</i> -C ₃ H ₁₁ CH=CHSC ₆ H ₅ <i>E:Z</i> ~ 1:1 (63)	157
						"	<i>n</i> -C ₄ H ₉ Li, TMEDA, C ₆ H ₁₄ , 0°	" <i>E:Z</i> ~ 1:1 (71)	157
							<i>n</i> -C ₄ H ₉ Li, THF, 0°	 (65)	157, 239
						"	<i>n</i> -C ₄ H ₉ Li, TMEDA, C ₆ H ₁₄ , 0°	" (68)	157
						<i>t</i> -C ₄ H ₉ COCH ₃	<i>n</i> -C ₄ H ₉ Li, THF, 0°	<i>t</i> -C ₄ H ₉ C(CH ₃)=CHSC ₆ H ₅ <i>E:Z</i> = 2:3 (55)	239
							"	CHSC ₆ H ₅ (75, 90)	239, 242
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CHSC ₆ H ₅ <i>E:Z</i> = 1:2 (71)	157, 239
						"	<i>n</i> -C ₄ H ₉ Li, TMEDA, C ₆ H ₁₄ , 0°	" <i>E:Z</i> ~ 1:1 (74)	157
						C ₆ H ₅ COCH ₃	<i>n</i> -C ₄ H ₉ Li, THF, 0°	C ₆ H ₅ C(CH ₃)=CHSC ₆ H ₅ <i>E:Z</i> ~ 1:1 (63)	157
						"	<i>n</i> -C ₄ H ₉ Li, TMEDA, C ₆ H ₁₄ , 0°	" <i>E:Z</i> ~ 1:1 (69)	157
							<i>n</i> -C ₄ H ₉ Li, THF, 0°	CHSC ₆ H ₅ (100)	242
						<i>n</i> -C ₇ H ₁₅ CHO	"	<i>n</i> -C ₇ H ₁₅ CH=CHSC ₆ H ₅ <i>E:Z</i> ~ 1:1 (64)	157
							"	CHSC ₆ H ₅ (90)	242
						Adamantanone	"	 (80)	239
						(C ₆ H ₅) ₂ CO	"	(C ₆ H ₅) ₂ C=CHSC ₆ H ₅ (82)	157

TABLE X. SULFUR-CONTAINING α -CARBANIONS (Continued)

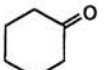
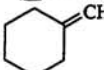
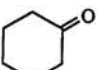
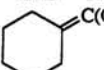
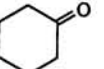
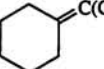
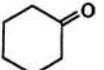
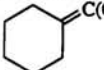
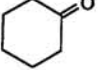
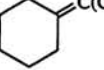
Silane					Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ^{2a}				
					HCON(CH ₃) ₂	"	(CH ₃) ₂ NCH=CHSC ₆ H ₅ E:Z = 100:0	(64) 243, 244
					<i>t</i> -C ₄ H ₉ CON(CH ₃) ₂	"	(CH ₃) ₂ NC(C ₄ H ₉ - <i>t</i>)=CHSC ₆ H ₅ E:Z = 20:80	(40) 243, 244
					C ₆ H ₅ CON(CH ₃) ₂	"	(CH ₃) ₂ NC(C ₆ H ₅)=CHSC ₆ H ₅ E:Z = 96:4	(44) 243, 244
					C ₆ H ₅ CON(CH ₂) ₂	"	(CH ₂) ₂ NC(C ₆ H ₅)=CHSC ₆ H ₅ E:Z = 80:20	(87) 243, 244
					C ₆ H ₅ CON(CH ₂) ₅	"	(CH ₂) ₅ NC(C ₆ H ₅)=CHSC ₆ H ₅ E:Z = 100:0	(55) ^c 243, 244
		C ₆ H ₅	H	SC ₆ H ₅	<i>n</i> -C ₅ H ₁₁ CHO	LiC ₁₀ H ₈ , THF, -78°	<i>n</i> -C ₅ H ₁₁ CH=CHSC ₆ H ₅ E:Z ~ 1:1	(75) 157, 241
						"	 =CHSC ₆ H ₅ (61)	157, 241
					C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CHSC ₆ H ₅ E:Z ~ 1:1	(70) 157, 241
		C ₆ H ₅	CH ₃	SC ₆ H ₅	(C ₆ H ₅) ₂ CO	"	(C ₆ H ₅) ₂ C=CHSC ₆ H ₅	(73) 157, 241
					<i>n</i> -C ₄ H ₉ CHO	"	<i>n</i> -C ₄ H ₉ CH=C(CH ₃)SC ₆ H ₅ E:Z ~ 1:1	(63) 157
					C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(CH ₃)SC ₆ H ₅ E:Z ~ 1:1	(64) 157, 241
		C ₆ H ₅	C ₂ H ₅	H	<i>n</i> -C ₄ H ₉ CHO	CH ₂ =C(SC ₆ H ₅)[Si(CH ₃) ₃], CH ₃ Li, TMEDA, Et ₂ O	C ₂ H ₅ C(SC ₆ H ₅)=CHC ₄ H ₉ - <i>n</i> E:Z ~ 1:1	(60) 157
					C ₆ H ₅ CHO	"	C ₂ H ₅ C(SC ₆ H ₅)=CHC ₆ H ₅ E:Z ~ 1:1	(65) 157
		C ₆ H ₅	<i>n</i> -C ₄ H ₉	SC ₆ H ₅	CH ₂ O	LiC ₁₀ H ₈ , THF, -78°	CH ₂ =C(C ₄ H ₉ - <i>n</i>)SC ₆ H ₅ (71)	157, 241
					<i>n</i> -C ₄ H ₉ CHO	"	<i>n</i> -C ₄ H ₉ CH=C(C ₄ H ₉ - <i>n</i>)SC ₆ H ₅ E:Z ~ 1:1	(58) 157, 241
						"	 =C(C ₄ H ₉ - <i>n</i>)SC ₆ H ₅ (51)	157, 241
					C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(C ₄ H ₉ - <i>n</i>)SC ₆ H ₅ E:Z ~ 1:1	(66) 157, 241
		C ₆ H ₅	<i>n</i> -C ₅ H ₁₁	H	(C ₆ H ₅) ₂ CO	CH ₂ =C(SC ₆ H ₅)[Si(CH ₃) ₃], <i>n</i> -C ₄ H ₉ Li, TMEDA, Et ₂ O	(C ₆ H ₅) ₂ C=C(C ₅ H ₁₁ - <i>n</i>)SC ₆ H ₅ (61)	157, 241
					CH ₃ CHO	"	CH ₃ CH=C(C ₅ H ₁₁ - <i>n</i>)SC ₆ H ₅ E:Z ~ 1:1	(47) 157
					<i>n</i> -C ₄ H ₉ CHO	"	<i>n</i> -C ₄ H ₉ CH=C(C ₅ H ₁₁ - <i>n</i>)SC ₆ H ₅ E:Z ~ 1:1	(52) 157
						"	 =C(C ₅ H ₁₁ - <i>n</i>)SC ₆ H ₅ (50)	157
					C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(C ₅ H ₁₁ - <i>n</i>)SC ₆ H ₅ E:Z ~ 1:1	(61) 157
					C ₆ H ₅ COCH ₃	"	C ₆ H ₅ (CH ₃)C=C(C ₅ H ₁₁ - <i>n</i>)SC ₆ H ₅ E:Z ~ 1:1	(43) 157
		C ₆ H ₅	C ₆ H ₅	H	CH ₂ O	<i>n</i> -C ₄ H ₉ Li, TMEDA, C ₆ H ₁₄ , 0°	CH ₂ =C(C ₆ H ₅)SC ₆ H ₅ (71)	157
					<i>n</i> -C ₄ H ₉ CHO	"	<i>n</i> -C ₄ H ₉ CH=C(C ₆ H ₅)SC ₆ H ₅ (63)	157
						"	 =C(C ₆ H ₅)SC ₆ H ₅ (47)	157
					C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(C ₆ H ₅)SC ₆ H ₅ (53)	157
		C ₆ H ₅	C ₆ H ₅ CH ₂	H	<i>n</i> -C ₄ H ₉ CHO	CH ₂ =C(SC ₆ H ₅)[Si(CH ₃) ₃], C ₆ H ₅ Li, TMEDA, Et ₂ O	<i>n</i> -C ₄ H ₉ CH=C(CH ₂ C ₆ H ₅)SC ₆ H ₅ E:Z ~ 1:1	(49) 157
						"	 =C(CH ₂ C ₆ H ₅)SC ₆ H ₅ (38)	157
					C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(CH ₂ C ₆ H ₅)SC ₆ H ₅ E:Z ~ 1:1	(51) 157
CH ₃		CH ₃	H	H	CH ₃ COC ₂ H ₅	KOC ₄ H ₉ - <i>t</i> (2 eq), DMSO	C ₂ H ₅ C(=CH ₂)CH(CH ₃)CH ₂ SCH ₃ (25)	247
					<i>i</i> -C ₃ H ₇ COCH ₃	KOC ₄ H ₉ - <i>t</i> , DMSO	CH ₃ C(=CH ₂)C(CH ₃) ₂ CH ₂ SCH ₃ (78)	247
					(C ₂ H ₅) ₂ CO	"	(C ₂ H ₅) ₂ C=CH \dot{S} (CH ₂) ₂ I ⁻ (9) + C ₂ H ₅ C(=CH ₂)CH(CH ₃)CH ₂ SCH ₃ (13)	247

TABLE X. SULFUR-CONTAINING α -CARBANIONS (Continued)


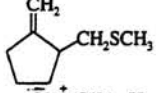
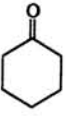
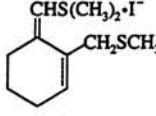

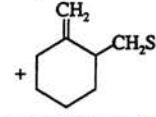
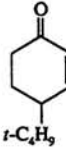


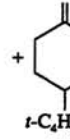
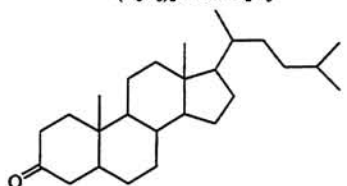
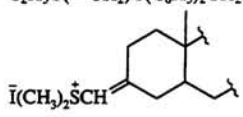
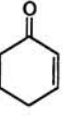
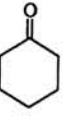
Silane					Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ^{2a}				
						"	 (19)	247
						"	 (12)	247
						"	 (21)	
					<i>i</i> -C ₄ H ₉ COCH ₃	KOC ₄ H ₉ - <i>t</i> (2 eq), DMSO	<i>i</i> -C ₄ H ₉ C(CH ₃)=CHS ⁺ (CH ₃) ₂ I ⁻ (9) + CH ₃ C(=CH ₂)CH(C ₃ H ₇ - <i>t</i>)CH ₂ SCH ₃ (6)	247
						"	 (9)	247
						"	 (18)	
					(C ₆ H ₅) ₂ CHCOCH ₃ (C ₆ H ₅) ₂ CHCOC ₂ H ₅	KOC ₄ H ₉ - <i>t</i> , DMSO	(C ₆ H ₅) ₂ CHC(CH ₃)=CHS ⁺ (CH ₃) ₂ I ⁻ (24)	247
						"	 (4)	247
O	-	C ₆ H ₅	H	H	CH ₂ =CHCHO	<i>n</i> -C ₄ H ₉ Li, THF, -70°	CH ₂ =CHCH=CHSOC ₆ H ₅ (67)	245
					"	<i>t</i> -C ₄ H ₉ Li, THF, -70°	<i>E</i> : <i>Z</i> = 1:1 (72)	245
					<i>i</i> -C ₃ H ₇ CHO	<i>n</i> -C ₄ H ₉ Li, THF, -70°	<i>i</i> -C ₃ H ₇ CH=CHSOC ₆ H ₅ (30)	245
					"	<i>t</i> -C ₄ H ₉ Li, THF, -70°	<i>E</i> : <i>Z</i> = 1:2 (66)	245
						"	CHSOC ₆ H ₅ (24)	245
						<i>n</i> -C ₄ H ₉ Li, THF, -70°	CHSOC ₆ H ₅ (66)	245
					"	<i>t</i> -C ₄ H ₉ Li, THF, -70°	"	(67) 245
					C ₆ H ₅ CHO	<i>n</i> -C ₄ H ₉ Li, THF, -70°	C ₆ H ₅ CH=CHSOC ₆ H ₅ (87)	245
					"	<i>t</i> -C ₄ H ₉ Li, THF, -70°	<i>E</i> : <i>Z</i> = 1:1 (81)	245
					C ₆ H ₅ CH=CHCHO	<i>n</i> -C ₄ H ₉ Li, THF, -70°	C ₆ H ₅ CH=CHCH=CHSOC ₆ H ₅ (70)	245

TABLE X. SULFUR-CONTAINING α -CARBANIONS (Continued)


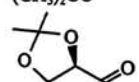
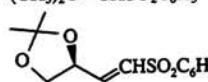
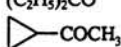
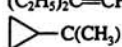
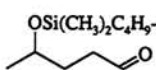
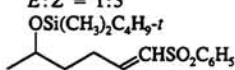




Silane					Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ^{2a}				
					Adamantanone	<i>t</i> -C ₄ H ₉ Li, THF, -70°	 CHSO ₂ C ₆ H ₅ (82)	245
					(C ₆ H ₅) ₂ CO	<i>n</i> -C ₄ H ₉ Li, THF, -70°	(C ₆ H ₅) ₂ C=CHSO ₂ C ₆ H ₅ (72)	245
					"	<i>t</i> -C ₄ H ₉ Li, THF, -70°	" (75)	245
O	—	C ₆ H ₄ - CH ₃ - <i>p</i>	H	H	(CH ₃) ₂ CO	<i>n</i> -C ₄ H ₉ Li, THF, -90°	(CH ₃) ₂ C=CHSO ₂ C ₆ H ₄ CH ₃ - <i>p</i> (15) ^d	246
					<i>n</i> -C ₃ H ₇ CHO	"	<i>n</i> -C ₃ H ₇ CH=CHSO ₂ C ₆ H ₄ CH ₃ - <i>p</i> (62) ^d	246
					<i>i</i> -C ₃ H ₇ CHO	"	<i>i</i> -C ₃ H ₇ CH=CHSO ₂ C ₆ H ₄ CH ₃ - <i>p</i> (55) ^d	246
					<i>i</i> -C ₄ H ₉ CHO	"	<i>i</i> -C ₄ H ₉ CH=CHSO ₂ C ₆ H ₄ CH ₃ - <i>p</i> (58) ^d	246
					<i>t</i> -C ₄ H ₉ CHO	"	<i>t</i> -C ₄ H ₉ CH=CHSO ₂ C ₆ H ₄ CH ₃ - <i>p</i> (50) ^d	246
					C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CHSO ₂ C ₆ H ₄ CH ₃ - <i>p</i> (65) ^d	246
					C ₆ H ₁₁ CHO	"	C ₆ H ₁₁ CH=CHSO ₂ C ₆ H ₄ CH ₃ - <i>p</i> (60) ^d	246
							<i>E:Z</i> = 1:2.9	
O	O	C ₆ H ₅	H	H	CH ₂ O	<i>n</i> -C ₄ H ₉ Li, THF, 0°	CH ₂ =CHSO ₂ C ₆ H ₅ (87)	157, 250
					CH ₃ CHO	"	CH ₃ CH=CHSO ₂ C ₆ H ₅ (81)	157, 250
					(CH ₃) ₂ CO	"	(CH ₃) ₂ C=CHSO ₂ C ₆ H ₅ (75)	157, 250
						<i>n</i> -C ₄ H ₉ Li, DME, -78°	 CHSO ₂ C ₆ H ₅ (72)	253
					<i>i</i> -C ₃ H ₇ CHO	"	<i>i</i> -C ₃ H ₇ CH=CHSO ₂ C ₆ H ₅ (70)	251, 253
							<i>E:Z</i> = 3:4	
							<i>E:Z</i> = 3:5	
					(CH ₃) ₂ CHCH ₂ COCH ₃	"	(CH ₃) ₂ CHCH ₂ C(CH ₃)=CHSO ₂ C ₆ H ₅ (65)	251, 253
					<i>n</i> -C ₄ H ₉ CHO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	<i>n</i> -C ₄ H ₉ CH=CHSO ₂ C ₆ H ₅ (85)	157, 250
					"	<i>n</i> -C ₄ H ₉ Li, DME, 0°	" (89)	157
							<i>E:Z</i> ~ 1:1	
					(C ₂ H ₅) ₂ CO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	(C ₂ H ₅) ₂ C=CHSO ₂ C ₆ H ₅ (60)	157, 250
						<i>n</i> -C ₄ H ₉ Li, DME, -78°	 C(CH ₃)=CHSO ₂ C ₆ H ₅ (79)	253
							<i>E:Z</i> = 1:3	
					OSi(CH ₃) ₂ C ₄ H ₉ - <i>t</i>	"	OSi(CH ₃) ₂ C ₄ H ₉ - <i>t</i> (74)	253
							 CHSO ₂ C ₆ H ₅	
							<i>E:Z</i> = 1:1	
					(<i>E</i>)-CH ₃ CH=C(CH ₃)CO- CH ₃	"	CH ₃ CH=C(CH ₃)C(CH ₃)=CHSO ₂ C ₆ H ₅ (87)	253
					<i>n</i> -C ₃ H ₁₁ CHO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	<i>n</i> -C ₃ H ₁₁ CH=CHSO ₂ C ₆ H ₅ (73)	157, 250
					"	<i>n</i> -C ₄ H ₉ Li, DME, 0°	" (79)	157
							<i>E:Z</i> ~ 1:1	
						<i>n</i> -C ₄ H ₉ Li, THF, 0°	CHSO ₂ C ₆ H ₅ (51)	157, 250
						"	 CHSO ₂ C ₆ H ₅ (83)	157, 250
						"	 CHSO ₂ C ₆ H ₅ (83)	157, 250
					"	<i>n</i> -C ₄ H ₉ Li, DME, 0°	" (86)	157
					"	<i>n</i> -C ₄ H ₉ Li, DME, -78°	" (92)	251, 253
					C ₆ H ₅ CHO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	C ₆ H ₅ CH=CHSO ₂ C ₆ H ₅ (79)	157, 250
					"	<i>n</i> -C ₄ H ₉ Li, DME, 0°	" (83)	157
							<i>E:Z</i> ~ 1:1	

TABLE X. SULFUR-CONTAINING α -CARBANIONS (Continued)

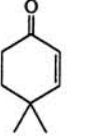
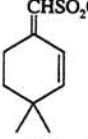
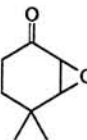
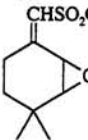
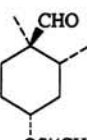
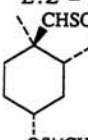
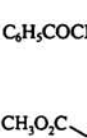
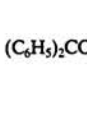
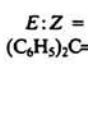
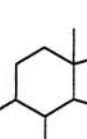
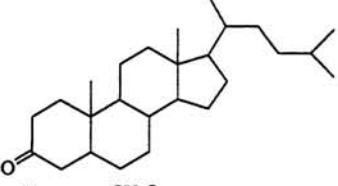
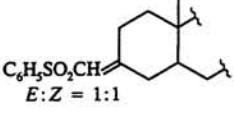
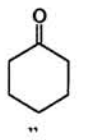
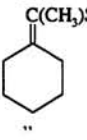
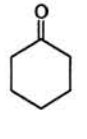
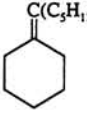
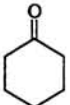

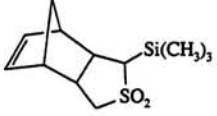
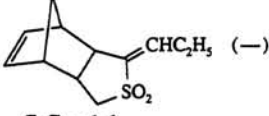
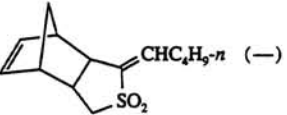
Silane					Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ^{2a}				
						<i>n</i> -C ₄ H ₉ Li, DME, -78°	 (81)	251, 253
						"	<i>E:Z</i> = 1:1  (84)	251, 253
						"	<i>E:Z</i> = 1:1  (92)	251, 253
					 OSi(CH ₃) ₂ C ₂ H ₅ - <i>t</i>	<i>n</i> -C ₄ H ₉ Li, THF, 0°	<i>E:Z</i> = 100:0 C ₆ H ₅ C(CH ₃)=CHSO ₂ C ₆ H ₅ (68)	157, 250
					 C ₆ H ₅ COCH ₃	<i>n</i> -C ₄ H ₉ Li, DME, -78°	<i>E:Z</i> ~ 1:1  (50)	251, 253
					 (C ₆ H ₅) ₂ CO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	<i>E:Z</i> = 1:1 (C ₆ H ₅) ₂ C=CHSO ₂ C ₆ H ₅ (71)	157, 250
						<i>n</i> -C ₄ H ₉ Li, DME, -78°	 (85), <i>E:Z</i> = 1:1	251, 253
O	O	C ₆ H ₅	CH ₃	H	CH ₂ O	<i>n</i> -C ₄ H ₉ Li, THF, 0°	CH ₂ =C(CH ₃)SO ₂ C ₆ H ₅ (64)	157, 250
					CH ₃ CHO	"	CH ₃ CH=C(CH ₃)SO ₂ C ₆ H ₅ (48)	157, 250
					<i>n</i> -C ₄ H ₉ CHO	"	<i>E:Z</i> ~ 1:1 <i>n</i> -C ₄ H ₉ CH=C(CH ₃)SO ₂ C ₆ H ₅ (35)	157, 250
					"	<i>n</i> -C ₄ H ₉ Li, DME, 0°	<i>E:Z</i> ~ 1:1 " (44)	157
					"	<i>n</i> -C ₄ H ₉ Li, THF, 0°	<i>E:Z</i> ~ 1:1 C(CH ₃)SO ₂ C ₆ H ₅ (32)	157, 250
						<i>n</i> -C ₄ H ₉ Li, DME, 0°		(39) 157
					C ₆ H ₅ CHO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	C ₆ H ₅ CH=C(CH ₃)SO ₂ C ₆ H ₅ (74)	157, 250
					"	<i>n</i> -C ₄ H ₉ Li, DME, 0°	<i>E:Z</i> ~ 1:1 " (78)	157
					(CH ₃) ₂ NCHO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	<i>E:Z</i> ~ 1:1 (CH ₃) ₂ NCH=C(CH ₃)SO ₂ C ₆ H ₅ (42)	242
					(CH ₂) ₃ NCHO	"	<i>E:Z</i> = 100:0 (CH ₂) ₃ NCH=C(CH ₃)SO ₂ C ₆ H ₅ (24)	242
					"	"	<i>E:Z</i> = 100:0	
O	O	C ₆ H ₅	<i>n</i> -C ₅ H ₁₁	H	(CH ₃) ₂ CO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	(CH ₃) ₂ C=C(C ₅ H ₁₁ - <i>n</i>)SO ₂ C ₆ H ₅ (34)	157
					<i>n</i> -C ₄ H ₉ CHO	"	<i>n</i> -C ₄ H ₉ CH=C(C ₅ H ₁₁ - <i>n</i>)SO ₂ C ₆ H ₅ (40)	157, 250
					"	<i>n</i> -C ₄ H ₉ Li, DME, 0°	<i>E:Z</i> ~ 1:1 " (42)	157
					"	<i>n</i> -C ₄ H ₉ Li, THF, 0°	<i>E:Z</i> ~ 1:1 C(C ₅ H ₁₁ - <i>n</i>)SO ₂ C ₆ H ₅ (19)	157, 250
								

TABLE X. SULFUR-CONTAINING α -CARBANIONS (Continued)

		Silane			Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ^{2a}				
					"	<i>n</i> -C ₄ H ₉ Li, DME, 0°	" (23)	157
					C ₆ H ₅ CHO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	C ₆ H ₅ CH=C(C ₅ H ₁₁ - <i>n</i>)SO ₂ C ₆ H ₅ (66)	157, 250
					CH ₂ O	"	<i>E</i> : <i>Z</i> ~ 1:1	
O	O	C ₆ H ₅	C ₆ H ₅	H	<i>n</i> -C ₄ H ₉ CHO	"	CH ₂ =C(C ₆ H ₅)SO ₂ C ₆ H ₅ (70)	157, 250
						"	<i>n</i> -C ₄ H ₉ CH=C(C ₆ H ₅)SO ₂ C ₆ H ₅ (61)	157, 250
						"	<i>E</i> : <i>Z</i> ~ 1:1	
						"	C(C ₆ H ₅)SO ₂ C ₆ H ₅ (23)	157, 250
					"	"		
					C ₆ H ₅ CHO	<i>n</i> -C ₄ H ₉ Li, DME, 0°	" (25)	157
					C ₆ H ₅ CHO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	C ₆ H ₅ CH=C(C ₆ H ₅)SO ₂ C ₆ H ₅ (82)	157, 250
					C ₆ H ₅ COCH ₃	"	<i>E</i> : <i>Z</i> ~ 1:1	
						"	C ₆ H ₅ C(CH ₃)=C(C ₆ H ₅)SO ₂ C ₆ H ₅ (65)	157, 250
						"	<i>E</i> : <i>Z</i> ~ 1:1	
					HCON(CH ₃) ₂	"	(CH ₃) ₂ NCH=C(C ₆ H ₅)SO ₂ C ₆ H ₅ (42)	244
					HCON(CH ₃) ₂	"	<i>E</i> : <i>Z</i> = 100:0	
						"	(CH ₃) ₂ NCH=C(C ₆ H ₅)SO ₂ C ₆ H ₅ (81)	244
						"	<i>E</i> : <i>Z</i> = 100:0	
					C ₂ H ₅ CHO	1. <i>n</i> -C ₄ H ₉ Li, THF 2. HMPA		254
						"	 (—)	
						"	<i>E</i> : <i>Z</i> = 1:1	
					<i>n</i> -C ₄ H ₉ CHO	"	 (—)	254
						"	<i>E</i> : <i>Z</i> = 1:1	

^a R² is a group which is displaced to form the alkyllithium.

^b No group is attached at this position.

^c The yield is determined by NMR.

^d This is the overall yield from the sulfoxide including the silylation step. Deprotonation for this latter step is achieved with LDA in THF at -90°.

TABLE XI. SELENIUM-CONTAINING α -SILYL CARBANIONS

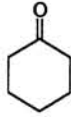
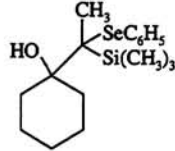
Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
$(\text{CH}_3)_3\text{SiCH}(\text{SeCH}_3)_2$	$n\text{-C}_{10}\text{H}_{21}\text{CHO}$	$n\text{-C}_4\text{H}_9\text{Li}$, THF	$\begin{array}{c} (\text{CH}_3)_3\text{Si} \quad \text{OH} \\ \quad \\ \text{H} \quad \text{H} \\ \quad \\ \text{CH}_3\text{Se} \quad \text{C}_{10}\text{H}_{21-n} \end{array} + \begin{array}{c} (\text{CH}_3)_3\text{Si} \quad \text{OH} \\ \quad \\ \text{CH}_3\text{Se} \quad \text{H} \\ \quad \\ \text{H} \quad \text{C}_{10}\text{H}_{21-n} \end{array}$ 35:65 (54)	257
$(\text{CH}_3)_3\text{SiC}(\text{CH}_3)(\text{SeCH}_3)_2$	"	"	$\begin{array}{c} (\text{CH}_3)_3\text{Si} \quad \text{OH} \\ \quad \\ \text{CH}_3 \quad \text{H} \\ \quad \\ \text{CH}_3\text{Se} \quad \text{C}_{10}\text{H}_{21-n} \end{array} + \begin{array}{c} (\text{CH}_3)_3\text{Si} \quad \text{OH} \\ \quad \\ \text{CH}_3\text{Se} \quad \text{H} \\ \quad \\ \text{CH}_3 \quad \text{C}_{10}\text{H}_{21-n} \end{array}$ 60:40 (50)	257
$(\text{CH}_3)_3\text{SiC}(\text{CH}_3)(\text{SeC}_6\text{H}_5)_2$		"	 (40)	256
	$n\text{-C}_6\text{H}_{13}\text{CHO}$	"	$n\text{-C}_6\text{H}_{13}\text{CHOHC}(\text{CH}_3)(\text{SeC}_6\text{H}_5)\text{Si}(\text{CH}_3)_3$ (40)	256
	$n\text{-C}_{10}\text{H}_{21}\text{CHO}$	"	$n\text{-C}_{10}\text{H}_{21}\text{CHOHC}(\text{CH}_3)(\text{SeC}_6\text{H}_5)\text{Si}(\text{CH}_3)_3$ (50)	256
	$n\text{-C}_9\text{H}_{19}\text{COCH}_3$	"	$n\text{-C}_9\text{H}_{19}\text{COHC}(\text{CH}_3)(\text{SeC}_6\text{H}_5)\text{Si}(\text{CH}_3)_3$ (35)	256

TABLE XII. PREPARATION OF VINYL SELENIDES

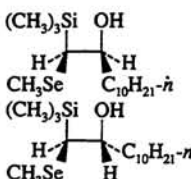
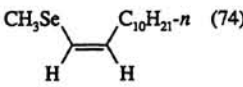
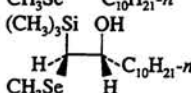
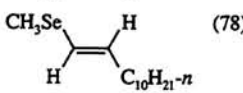
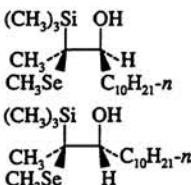
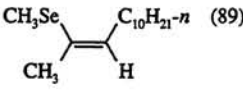
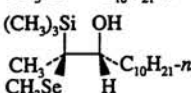
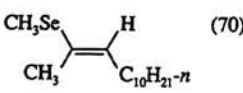
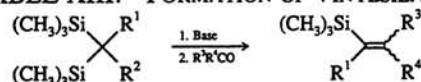
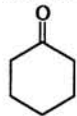
Silane	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	KOC ₄ H ₉ -t, THF, 55°	 (74)	257
	"	 (78)	257
C_{13} 	"	 (89)	257
	"	 (70)	257

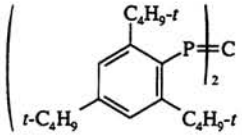


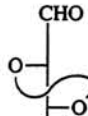


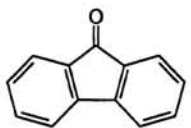
TABLE XIII. FORMATION OF VINYLSILANES



Silane		Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
R ¹	R ²				
C ₁					
H	H	CH ₂ O	<i>t</i> -C ₄ H ₉ Li, THF, HMPA, -78°	(CH ₃) ₃ SiCH=CH ₂ (45)	170
		CH ₂ =CHCHO	<i>n</i> -C ₄ H ₉ Li, TMEDA, Et ₂ O	(CH ₃) ₃ SiCH=CHCH=CH ₂ (13)	103
		<i>n</i> -C ₃ H ₇ CHO	<i>t</i> -C ₄ H ₉ Li, THF, HMPA, -78°	(CH ₃) ₃ SiCH=CHC ₆ H ₅ - <i>n</i> (25) ^a	170
		C ₆ H ₅ CHO	"	(CH ₃) ₃ SiCH=CHC ₆ H ₅ (70)	170, 259
		C ₆ H ₅ CH=CHCHO	"	(CH ₃) ₃ SiCH=CHCH=CHC ₆ H ₅ (37) E:Z = 1.4:1	170
H	SC ₆ H ₅	(C ₆ H ₅) ₂ CO	LiC ₁₀ H ₈ , THF, -78°	(CH ₃) ₃ SiCH=C(C ₆ H ₅) ₂ (65)	170, 259
			"	(CH ₃) ₃ SiCH (0)	241
		C ₆ H ₅ CHO	"	(CH ₃) ₃ SiCH=CHC ₆ H ₅ (72) ^a	241
		(C ₆ H ₅) ₂ CO	"	(CH ₃) ₃ SiCH=C(C ₆ H ₅) ₂ (63)	241
C ₂					
CH ₃	SC ₆ H ₅	CH ₂ O	"	(CH ₃) ₃ SiC(CH ₃)=CH ₂ (71)	241
		C ₆ H ₅ CHO	"	(CH ₃) ₃ SiC(CH ₃)=CHC ₆ H ₅ (69) ^a	241
C ₃					
<i>n</i> -C ₄ H ₉	SC ₆ H ₅	(C ₆ H ₅) ₂ CO	"	(CH ₃) ₃ SiC(CH ₃)=C(C ₆ H ₅) ₂ (57)	241
		H ₂ CO	"	(CH ₃) ₃ SiC(C ₄ H ₉ - <i>n</i>)=CH ₂ (73)	241
		C ₆ H ₅ CHO	"	(CH ₃) ₃ SiC(C ₄ H ₉ - <i>n</i>)=CHC ₆ H ₅ (62) ^a	241
		(C ₆ H ₅) ₂ CO	(<i>n</i> -C ₄ H ₉) ₃ SnLi, THF, -78° LiC ₁₀ H ₈ , THF, -78°	" (74) ^a (CH ₃) ₃ SiC(C ₄ H ₉ - <i>n</i>)=C(C ₆ H ₅) ₂ (48)	164 241
C ₄					
<i>n</i> -C ₃ H ₁₁	H	CH ₂ O	[(CH ₃) ₃ Si] ₂ C=CH ₂ , <i>n</i> -C ₄ H ₉ Li	(CH ₃) ₃ SiC(C ₃ H ₁₁ - <i>n</i>)=CH ₂ (73)	240, 259
		C ₆ H ₅ CHO	"	(CH ₃) ₃ SiC(C ₃ H ₁₁ - <i>n</i>)=CHC ₆ H ₅ (66)	240, 259
	H	CH ₂ O	[(CH ₃) ₃ Si] ₂ C=CH ₂ , <i>s</i> -C ₄ H ₉ Li	(CH ₃) ₃ SiC(CH ₂ C ₄ H ₉ - <i>s</i>)=CH ₂ (64)	240, 259
		CH ₂ O	[(CH ₃) ₃ Si] ₂ C=CH ₂ , <i>t</i> -C ₄ H ₉ Li	(CH ₃) ₃ SiC(CH ₂ C ₄ H ₉ - <i>t</i>)=CH ₂ (71)	240, 259
		C ₆ H ₅ CHO	"	(CH ₃) ₃ SiC(CH ₂ C ₄ H ₉ - <i>t</i>)=CHC ₆ H ₅ (64)	240, 259
C ₆ H ₅ CH=CHCHO	"	"	E:Z = 5:7 (CH ₃) ₃ SiC(C ₄ H ₉ - <i>t</i>)=CHCH=CHC ₆ H ₅ (61)	240, 259	
	"	"	E:Z = 2:5		
C ₇					
C ₆ H ₅	SC ₆ H ₅	CH ₂ O	LiC ₁₀ H ₈ , THF, -78°	(CH ₃) ₃ SiC(C ₆ H ₅)=CH ₂ (66)	241
C ₈					
C ₆ H ₅ CH ₂	SC ₆ H ₅	C ₆ H ₅ CHO	(<i>n</i> -C ₄ H ₉) ₃ SnLi	(CH ₃) ₃ SiC(CH ₂ C ₆ H ₅)=CHC ₆ H ₅ (76) ^a	164
C ₁₂					
<i>t</i> -C ₄ H ₉ (C ₆ H ₅)CH	H	CH ₂ O	[(CH ₃) ₃ Si] ₂ C=CHC ₄ H ₉ - <i>t</i> , C ₆ H ₅ Li	(CH ₃) ₃ SiC[CH(C ₆ H ₅)C ₄ H ₉ - <i>t</i>]=CH ₂ (81)	240



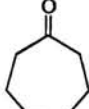

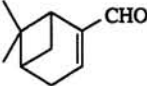

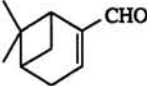
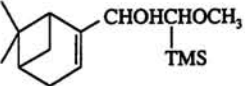
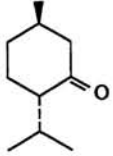
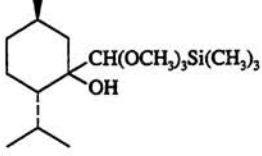
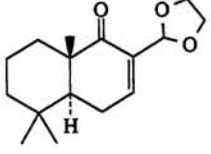
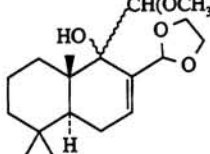
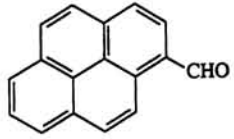
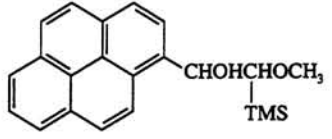
^a The E:Z isomer ratio is not given.

TABLE XIV. PHOSPHORUS-CONTAINING α -SILYL CARBANIONS

Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 $o,o,p-(t-C_4H_9)_3C_6H_2PHSi(CH_3)_3$	$o,o,p-(t-C_4H_9)_3C_6H_2PCO$	1. $t-C_4H_9Li$, Et_2O 2. $(CH_3)_3SiCl$	 (35)	266
C_1 $(CH_3)_3SiCH_2P(C_6H_5)_2$	C_6H_5CHO	$n-C_4H_9Li$, THF, 0°	$(C_6H_5)_2PCH=CHC_6H_5$ (53) $E:Z = 1:1$	3
$(CH_3)_3SiCH_2P(C_6H_5)_3^+I^-$	$(C_6H_5)_2CO$	"	$(C_6H_5)_2PCH=C(C_6H_5)_2$ (65)	3
$(CH_3)_3Si(CH=P(C_6H_5)_3)$	$(C_6H_5)_2CO$	C_6H_5Li	$(C_6H_5)_2C=C=C(C_6H_5)_2$ (20-35)	262
	$CH_2=CHCOCH_3$	Et_2O , -63°	$CH_2=CHC(CH_3)=CHP(C_6H_5)_3 \cdot OSi(CH_3)_3$ (50) ^a	263
	$CH_3CH=CHCHO$	"	$CH_3CH=CHCH=CHP(C_6H_5)_3 \cdot OSi(CH_3)_3$ (86) ^a	263
	$C_6H_5CH=CHCHO$	"	$C_6H_5CH=CHCH=CHP(C_6H_5)_3 \cdot OSi(CH_3)_3$ (100) ^a	263
	$C_6H_5CH=C(C_6H_5)CHO$	"	$C_6H_5CH=C(C_6H_5)CH=CHP(C_6H_5)_3 \cdot OSi(CH_3)_3$ (<5) ^a	263
$(CH_3)_3SiCH_2PS(C_6H_5)_2$ $(CH_3)_3SiCH_2PO(OCH_3)_2$	$(C_6H_5)_2CO$ CHO 	$n-C_4H_9Li$, THF, 0° "	$(C_6H_5)_2PSCH=C(C_6H_5)_2$ (80) $CH=CHPO(OCH_3)_2$ (-)  $E:Z = 1:1$	3 264
		"	$CH=CHPO(OCH_3)_2$ (-)	264
$(CH_3)_3SiCH_2PO(OC_2H_5)_2$	$(CH_3)_2CO$ $i-C_3H_7CHO$ 	$n-C_4H_9Li$, THF "	$E:Z = 2:1$ $(C_2H_5O)_2POCH=C(CH_3)_2$ (55) $(C_2H_5O)_2POCH=CHC_3H_7-i$ (92) $E:Z = 1:2.4$  + (65)	239 239 239
	C_6H_5CHO	"	$(C_2H_5O)_2POCH=CHC_6H_5$ (63) $E:Z = 100:0$	239
		"	$CHPO(OC_2H_5)_2$ (42)	239
	$(C_6H_5)_2CO$	"	$(C_2H_5O)_2POCH=C(C_6H_5)_2$ (83)	239
C_4 $(CH_3)_3SiCH_2CH(C_2H_5)PO(C_6H_5)_2$	C_6H_5CHO	$n-C_4H_9Li$, THF, -50°	$(C_6H_5)_2POCH(C_2H_5)CH=CHC_6H_5$ (-)	98

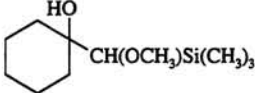
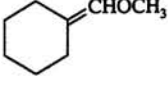
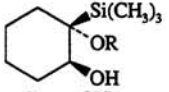
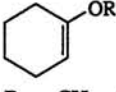
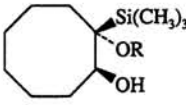
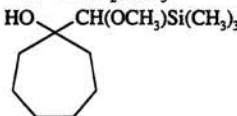
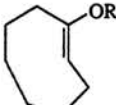
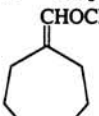
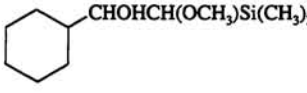
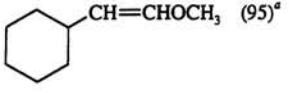
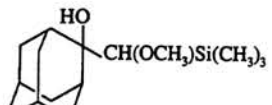
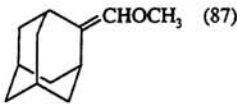
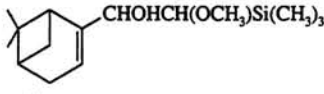
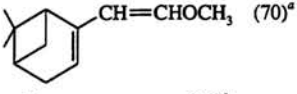
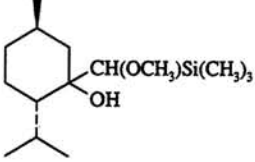
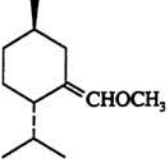
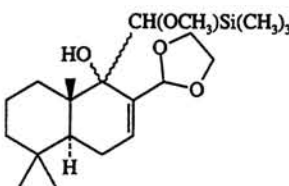
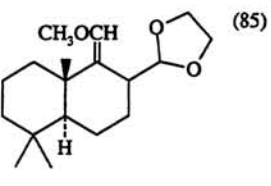
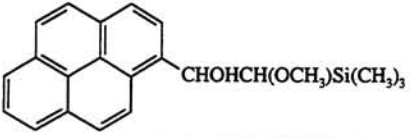
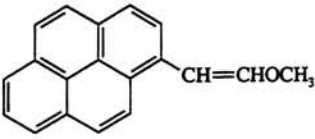
^a The yield is determined by NMR spectroscopy.

TABLE XV. REACTIONS OF OXYGEN-CONTAINING α -SILYL CARBANIONS

Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
$(\text{CH}_3)_3\text{SiCH}_2\text{OCH}_3$		$s\text{-C}_4\text{H}_9\text{Li}$, THF, -78°	 (73)	276, 277
		"	 (65)	277
	$\text{C}_6\text{H}_{11}\text{CHO}$ Adamantanone	"	$\text{C}_6\text{H}_{11}\text{CHOHCH(OCH}_2\text{)Si(CH}_3\text{)}_3$ (80)	276, 277
		"	 (89)	277
		"	 (85)	277
		"	 (89)	277
		"	 (73)	278
	"	 (55)	277	
$\text{C}_6\text{H}_5\text{CH(OCH}_3\text{)Si(CH}_3\text{)}_3$	$\text{C}_6\text{H}_5\text{CHO}$	$n\text{-C}_4\text{H}_9\text{Li}$, THF, 0°	$\text{C}_6\text{H}_5\text{CH=C(OCH}_3\text{)C}_6\text{H}_5$ (83) ^a	279
	"	$n\text{-C}_6\text{H}_5\text{Li}$, HMPA, 0°	" (41) ^a	279

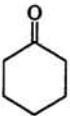
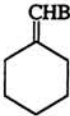
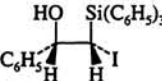
^a The product is a mixture of isomers.

TABLE XVI. ELIMINATION OF β -HYDROXYSILANES TO GIVE VINYL ETHERS

Silane	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇ 	KH, THF, 60°	 (85)	276, 277
 R = CH ₃ R = CH ₂ SCH ₃	NaH, DMF	 R = CH ₃ (>98) R = CH ₂ SCH ₃ (90)	30 74
C ₈  R = CH ₃ R = CH ₂ SCH ₃ 	KH, THF	 R = CH ₃ (—) R = CH ₂ SCH ₃ (—)  (79)	74 277
	"	 (95) ^a	276, 277
	"	 (87)	276, 277
	"	 (70) ^a	277
	"	 (86) ^a	276
C ₁₅ 	KH, THF, 0°	 (85)	278
C ₁₇ 	KH, THF, 60°	 (70) ^a	277

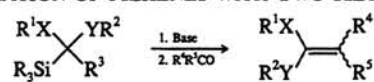
^a The product is a mixture of isomers.

TABLE XVII. OTHER MISCELLANEOUS α -SILYL CARBANIONS CONTAINING A HETEROATOM SUBSTITUENT

Silane	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
$(\text{CH}_3)_3\text{SiCH}_2\text{Sn}(\text{C}_4\text{H}_9-n)_3$	$\text{C}_6\text{H}_5\text{CHO}$	KDA, THF, -78°	$\text{C}_6\text{H}_5\text{CH}=\text{CHSn}(\text{C}_4\text{H}_9-n)_3$ $E:Z = 55:45$	(35) 260
$(\text{CH}_3)_3\text{SiCH}_2\text{B}[\text{OC}(\text{CH}_3)_2]_2$		LiTMP, THF, 0°	 $\text{CHB}[\text{OC}(\text{CH}_3)_2]_2$ (87)	280
	$\text{C}_6\text{H}_5\text{CHO}$	"	$\text{C}_6\text{H}_5\text{CH}=\text{CHB}[\text{OC}(\text{CH}_3)_2]_2$ $E:Z = 1:2$	(84) 280
	$n\text{-C}_6\text{H}_{13}\text{CHO}$	"	$n\text{-C}_6\text{H}_{13}\text{CH}=\text{CHB}[\text{OC}(\text{CH}_3)_2]_2$ $E:Z = 1:2$	(73) 280
	$(n\text{-C}_4\text{H}_9)_2\text{CO}$	"	$(n\text{-C}_4\text{H}_9)_2\text{C}=\text{CHB}[\text{OC}(\text{CH}_3)_2]_2$ (74)	280
$(\text{CH}_3)_3\text{SiCH}_2\text{BMes}_2$	$\text{C}_6\text{H}_5\text{CHO}$	1. MesLi, THF 2. H_2O_2 , NaOH	$\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ (95)	283
	$(\text{C}_6\text{H}_5)_2\text{CO}$	MesLi	$(\text{C}_6\text{H}_5)_2\text{C}=\text{CHSi}(\text{CH}_3)_3$ (55) + $(\text{C}_6\text{H}_5)_2\text{C}=\text{CH-BMes}_2$ (45) ^a	283
$(\text{C}_6\text{H}_5)_3\text{SiCH}_2\text{I}$	$\text{C}_6\text{H}_5\text{CHO}$	1. $\text{C}_6\text{H}_5\text{Li}$, THF 2. $\text{C}_6\text{H}_5\text{Li}$	$\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$ $E:Z \sim 0:100$	(36) 272
	"	1. $\text{C}_6\text{H}_5\text{Li}$, Et_2O , -60° 2. CH_3OH , -65°	 (41)	271

^a The product is isolated as the aldehyde after oxidative workup.

TABLE XVIII. FORMATION OF ALKENES WITH TWO HETEROATOM SUBSTITUENTS



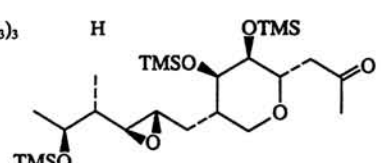
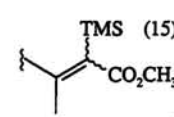
Silane							Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ²	R ³					
C ₁	CO ₂	Si	CH ₃	CH ₃	(CH ₃) ₃	H		LDA, THF, -78°	 (15) ^d E:Z = 3:1	45
	CO ₂	Si	<i>i</i> -C ₄ H ₉	CH ₃	(CH ₃) ₃	H	CH ₂ O CH ₃ CHO C ₂ H ₅ CHO	" " " " KDA, THF, -78° 1. LDA, THF, -78° 2. MgBr ₂ ·OEt ₂ 1. LDA, THF, -78° 2. (C ₂ H ₅) ₂ AlCl LDA, THF, -78°	CH ₂ =C[Si(CH ₃) ₃]CO ₂ C ₄ H ₉ - <i>t</i> (35) CH ₃ CH=C[Si(CH ₃) ₃]CO ₂ C ₄ H ₉ - <i>t</i> (58) C ₂ H ₅ CH=C[Si(CH ₃) ₃]CO ₂ C ₄ H ₉ - <i>t</i> (51) E:Z = 1:1 " E:Z = 1:2 " E:Z = 1:1 " E:Z = 2:1 " E:Z = 1:1.2 (<i>E</i>)-CH ₃ CH=CHCH=C[Si(CH ₃) ₃]- CO ₂ C ₄ H ₉ - <i>t</i> (85) ^{b,c} <i>i</i> -C ₃ H ₇ CH=C[Si(CH ₃) ₃]CO ₂ C ₄ H ₉ - <i>t</i>	286 286 462 (91) 46 (78) 46 (94) 46 (75) 46 286 286 (74) ^c (82) 46 (82) 46
							(<i>E</i>)-CH ₃ CH=CH- CHO <i>i</i> -C ₃ H ₇ CHO	" " " " KDA, THF, -78°	" " " " E:Z = 1:6.5 " E:Z < 1:100	

TABLE XVIII. FORMATION OF ALKENES WITH TWO HETEROATOM SUBSTITUENTS (Continued)

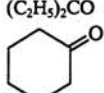
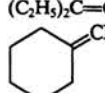
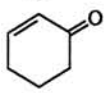
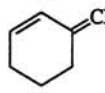
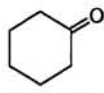
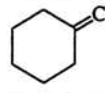
Silane						Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
X ^a	Y	R	R ¹	R ²	R ³					
						"	1. LDA, THF, -78°	"	(82)	46
						"	2. MgBr ₂ ·OEt ₂	E:Z = 3.5:1	(82)	46
						"	1. LDA, THF, -78°	"	(82)	46
						"	2. (C ₂ H ₅) ₂ AlCl	E:Z = 4:1	(82)	46
						<i>t</i> -C ₄ H ₉ CHO	LDA, THF, -78°	<i>t</i> -C ₄ H ₉ CH=C[Si(CH ₃) ₃]CO ₂ C ₄ H ₉ - <i>t</i>	(51)	46
						"	KDA, THF, -78°	"	(84)	46
						"	"	E:Z < 1:100	(84)	46
						"	1. LDA, THF, -78°	"	(93)	46
						"	2. MgBr ₂ ·OEt ₂	E:Z = 1:30	(93)	46
						"	1. LDA, THF, -78°	"	(81)	46
						"	2. (C ₂ H ₅) ₂ AlCl	E:Z = 9:1	(81)	46
						C ₆ H ₅ CHO	LDA, THF, -78°	C ₆ H ₅ CH=C[Si(CH ₃) ₃]CO ₂ C ₄ H ₉ - <i>t</i>	(65) ^c	286
						"	"	"	(88)	46
						"	"	E:Z = 1:9.4	(88)	46
						"	KDA, THF, -78°	"	(91)	46
						"	"	E:Z = 1:17	(91)	46
						"	1. LDA, THF, -78°	"	(83)	46
						"	2. MgBr ₂ ·OEt ₂	E:Z = 1:3.4	(83)	46
						"	1. LDA, THF, -78°	"	(84)	46
						"	2. (C ₂ H ₅) ₂ AlCl	E:Z = 2.5:1	(84)	46
CO ₂	Sn	CH ₃	<i>t</i> -C ₄ H ₉	(<i>n</i> -C ₄ H ₉) ₃	H	CH ₂ O	LDA, THF, HMPA, -23° to -78°	CH ₂ =C[Sn(C ₄ H ₉ - <i>n</i>) ₃]CO ₂ C ₄ H ₉ - <i>t</i>	(26)	287
						<i>n</i> -C ₃ H ₇ CHO	"	<i>n</i> -C ₃ H ₇ CH=C[Sn(C ₄ H ₉ - <i>n</i>) ₃]CO ₂ C ₄ H ₉ - <i>t</i>	(51)	287
						"	"	E:Z = 46:54	(51)	287
						<i>i</i> -C ₃ H ₇ CHO	"	<i>i</i> -C ₃ H ₇ CH=C[Sn(C ₄ H ₉ - <i>n</i>) ₃]CO ₂ C ₄ H ₉ - <i>t</i>	(20)	287
						"	"	E:Z = 69:31	(20)	287
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C[Sn(C ₄ H ₉ - <i>n</i>) ₃]CO ₂ C ₄ H ₉ - <i>t</i>	(70)	287
						"	"	E:Z = 45:55	(70)	287
						"	KDA, THF, -78°	"	(72)	260
						"	"	E:Z = 1:1	(72)	260
						<i>p</i> -CH ₃ C ₆ H ₄ CHO	LDA, THF, HMPA, -23° to -78°	<i>p</i> -CH ₃ C ₆ H ₄ CH=C[Sn(C ₄ H ₉ - <i>n</i>) ₃]CO ₂ -C ₄ H ₉ - <i>t</i>	(31)	287
						"	"	E:Z = 37:63	(31)	287
						<i>p</i> -ClC ₆ H ₄ CHO	"	<i>p</i> -ClC ₆ H ₄ CH=C[Sn(C ₄ H ₉ - <i>n</i>) ₃]CO ₂ C ₄ H ₉ - <i>t</i>	(41)	287
						"	"	E:Z = 48:52	(41)	287
						(C ₆ H ₅) ₂ CO	KDA, THF, -78°	(C ₆ H ₅) ₂ C=C[Sn(C ₄ H ₉ - <i>n</i>) ₃]CO ₂ C ₄ H ₉ - <i>t</i>	(46)	260
CO ₂	Br	CH ₃	<i>t</i> -C ₄ H ₉	—	—	<i>i</i> -C ₄ H ₉ CHO	1. LDA, THF, -78°	<i>i</i> -C ₄ H ₉ CH=CBrCO ₂ C ₄ H ₉ - <i>t</i>	(37)	289
						"	2. SOCl ₂ , 0°	"	(37)	289
						(C ₂ H ₅) ₂ CO	"	(C ₂ H ₅) ₂ C=CBrCO ₂ C ₄ H ₉ - <i>t</i>	(40)	289
							"	 CBrCO ₂ C ₄ H ₉ - <i>t</i>	(66)	289
							"	 CBrCO ₂ C ₄ H ₉ - <i>t</i>	(25)	289
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CBrCO ₂ C ₄ H ₉ - <i>t</i>	(57)	289
						C ₆ H ₅ CH=CHCHO	"	C ₆ H ₅ CH=CHCH=CBrCO ₂ C ₄ H ₉ - <i>t</i>	(44)	289
						"	"	"	(44)	289
CO ₂	Cl	CH ₃	<i>t</i> -C ₄ H ₉	—	H	<i>n</i> -C ₁₅ H ₃₁ CHO	"	<i>n</i> -C ₁₅ H ₃₁ CH=CBrCO ₂ C ₄ H ₉ - <i>t</i>	(47)	289
						C ₂ H ₅ CHO	LDA, THF, -78°	C ₂ H ₅ CH=CClCO ₂ C ₄ H ₉ - <i>t</i>	(55)	288
						"	"	E:Z = 49:51	(55)	288
						<i>i</i> -C ₃ H ₇ CHO	"	<i>i</i> -C ₃ H ₇ CH=CClCO ₂ C ₄ H ₉ - <i>t</i>	(25)	288
						"	"	E:Z = 36:64	(25)	288
						CH ₂ =CH-(CH ₂) ₂ CHO	"	CH ₂ =CH(CH ₂) ₂ CH=CClCO ₂ C ₄ H ₉ - <i>t</i>	(49)	288
						"	"	E:Z = 34:66	(49)	288
						<i>i</i> -C ₃ H ₇ COCH ₃	"	<i>i</i> -C ₃ H ₇ C(CH ₃)=CClCO ₂ C ₄ H ₉ - <i>t</i>	(17)	288
						"	"	E:Z = 18:82	(17)	288
							"	 CClCO ₂ C ₄ H ₉ - <i>t</i>	(44)	288
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CClCO ₂ C ₄ H ₉ - <i>t</i>	(55)	288
						"	"	E:Z = 46:54	(55)	288

TABLE XVIII. FORMATION OF ALKENES WITH TWO HETEROATOM SUBSTITUENTS (Continued)

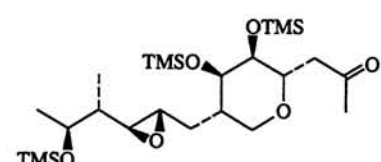
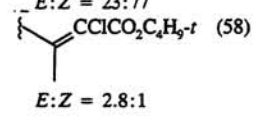
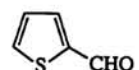
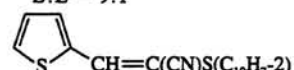
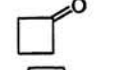
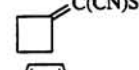
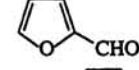
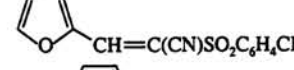
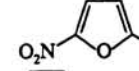
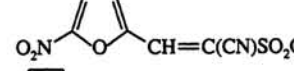
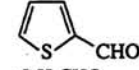
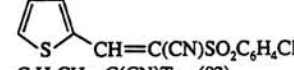
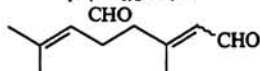
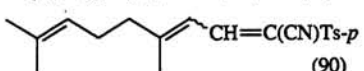
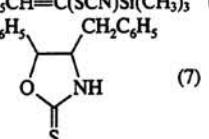
X	Y	Silane			R ²	R ³	Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
		R	R ¹	R ²							
							C ₆ H ₁₁ CHO	"	C ₆ H ₁₁ CH=CClCO ₂ C ₄ H ₉ - <i>t</i>	(44) 288	
							C ₆ H ₅ CH ₂ CHO	"	C ₆ H ₅ CH ₂ CH=CClCO ₂ C ₄ H ₉ - <i>t</i>	(40) 288	
								"		(58) 45	
									E:Z = 2.8:1		
194	NC	N	CH ₃	—	CH ₃ (C ₆ H ₅)	H	CH ₂ O <i>n</i> -C ₃ H ₇ CHO <i>n</i> -C ₃ H ₁₁ CHO	LDA KH, THF 1. KH, THF 2. Heat	CH ₂ =C(CN)N(CH ₃)C ₆ H ₅ (83) <i>n</i> -C ₃ H ₇ CH=C(CN)N(CH ₃)C ₆ H ₅ (56) <i>n</i> -C ₃ H ₁₁ CH=C(CN)N(CH ₃)C ₆ H ₅ (53)	290 291 291	
	NC	S	CH ₃	—	<i>p</i> -ClC ₆ H ₄	H	C ₆ H ₅ CHO (C ₆ H ₅) ₂ CO <i>t</i> -C ₄ H ₉ CHO	"	C ₆ H ₅ CH=C(CN)N(CH ₃)C ₆ H ₅ (100) (C ₆ H ₅) ₂ C=C(CN)N(CH ₃)C ₆ H ₅ (68) <i>t</i> -C ₄ H ₉ CH=C(CN)SC ₆ H ₄ Cl- <i>p</i> (53)	291 291 292	
								"	E:Z = 100:0 ^a	(70) 292	
								"	C ₆ H ₅ CH=C(CN)SC ₆ H ₄ Cl- <i>p</i> (66) <i>p</i> -ClC ₆ H ₄ CH=C(CN)SC ₆ H ₄ Cl- <i>p</i> (78)	292 292	
	NC	S	CH ₃	—	<i>p</i> -CH ₃ C ₆ H ₄	H	C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(CN)SC ₆ H ₄ CH ₃ - <i>p</i>	(74) 292	
								"	E:Z = 1:3		
	NC	S	CH ₃	—	2-C ₁₀ H ₇	H	<i>t</i> -C ₄ H ₉ CHO	"	<i>t</i> -C ₄ H ₉ CH=C(CN)S(C ₁₀ H ₇ -2)	(52) 292	
								"	E:Z = 9:1	(82) 292	
									"		(70) 292
								C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(CN)S(C ₁₀ H ₇ -2)	(74) 292
							<i>p</i> -ClC ₆ H ₄ CHO	"	<i>p</i> -ClC ₆ H ₄ CH=C(CN)S(C ₁₀ H ₇ -2)	(50) 292	
							C ₆ H ₁₁ CHO	"	C ₆ H ₁₁ CH=C(CN)S(C ₁₀ H ₇ -2)	(70) 292	
NC	SO ₂	CH ₃	—	<i>p</i> -CH ₃ C ₆ H ₄	H	CCl ₃ CHO	<i>n</i> -C ₄ H ₉ Li, THF, -70°	CCl ₃ CH=C(CN)Ts (25) C(CN)SO ₂ C ₆ H ₄ CH ₃ - <i>p</i> (64)	293 293		
							"		(88) 293		
							"		(10) 293		
							"		(87) 293		
							"		(82) 293		
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(CN)Ts (82)	293		
						<i>p</i> -ClC ₆ H ₄ CHO	"	<i>p</i> -ClC ₆ H ₄ CH=C(CN)Ts (85)	293		
						<i>p</i> -O ₂ NC ₆ H ₄ CHO	"	<i>p</i> -O ₂ NC ₆ H ₄ CH=C(CN)Ts (55)	293		
						<i>p</i> -CH ₃ OC ₆ H ₄ CHO	"	<i>p</i> -CH ₃ OC ₆ H ₄ CH=C(CN)Ts (93)	293		
						<i>p</i> -(CH ₃) ₂ NC ₆ H ₄ -CHO	"	<i>p</i> -(CH ₃) ₂ NC ₆ H ₄ CH=C(CN)Ts (76)	293		
							"		(90) 293		
						(<i>E</i>)-C ₆ H ₅ CH=CH-CHO	"	(<i>E</i>)-C ₆ H ₅ CH=CHCH=C(CN)Ts (83)	293		
NCS	Si	CH ₃	—	(CH ₃) ₃	Si(CH ₃) ₃	C ₆ H ₅ CHO	1. (C ₄ H ₉) ₄ N ⁺ F ⁻ , THF 2. H ₂ O	C ₆ H ₅ CH=C(SCN)Si(CH ₃) ₃ (26) + 	(7) 238		

TABLE XVIII. FORMATION OF ALKENES WITH TWO HETEROATOM SUBSTITUENTS (Continued)

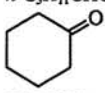
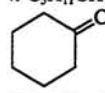
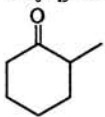
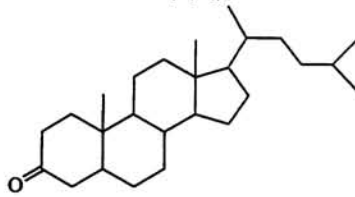
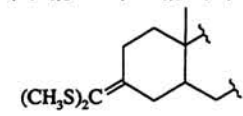
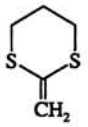
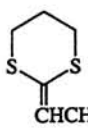
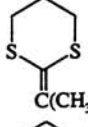
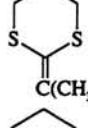
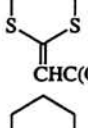
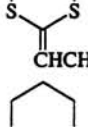
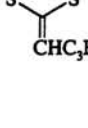

Silane						Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ²	R ³				
S	S	CH ₃	CH ₃	CH ₃	H	CH ₂ O	<i>n</i> -C ₄ H ₉ Li, THF, -60°	CH ₂ =C(SCH ₃) ₂ (86)	308
						<i>n</i> -C ₄ H ₉ CHO	"	<i>n</i> -C ₄ H ₉ CH=C(SCH ₃) ₂ (80)	308
						<i>n</i> -C ₅ H ₁₁ CHO	"	<i>n</i> -C ₅ H ₁₁ CH=C(SCH ₃) ₂ (82)	313
							"	 (80)	308
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(SCH ₃) ₂ (85)	313
						<i>n</i> -C ₆ H ₁₃ CHO	"	<i>n</i> -C ₆ H ₁₃ CH=C(SCH ₃) ₂ (84)	313
							"	C(SCH ₃) ₂ (54)	313
						C ₆ H ₅ COCH ₃	"	C ₆ H ₅ C(CH ₃)=C(SCH ₃) ₂ (57)	313
						<i>m,p</i> -(CH ₃ O) ₂ C ₆ H ₃ -CHO	"	<i>m,p</i> -(CH ₃ O) ₂ C ₆ H ₃ CH=C(SCH ₃) ₂ (88)	313
						(C ₆ H ₅) ₂ CO	"	(C ₆ H ₅) ₂ C=C(SCH ₃) ₂ (-)	308, 314
							"	 (58)	313
S	S	CH ₃	-(CH ₂) ₅ -		H	CH ₂ O	"	 (71)	308, 314
						CH ₃ CHO	"	 (45-69)	304, 307, 308
						(CH ₃) ₂ CO	"	 (45-75)	303, 304, 307, 308
						CH ₃ COCH ₂ OTHP	"	 (-)	307
						CH ₂ =C(OCH ₃)-CHO	-	 (70)	311
						(<i>E</i>)-CH ₃ CH=CH-CHO	<i>n</i> -C ₄ H ₉ Li, THF, -60°	 (93) ^d	308
						<i>n</i> -C ₃ H ₇ CHO	"	 (67-75)	303, 304, 308
							"	 CHC ₃ H _{7-n}	

TABLE XVIII. FORMATION OF ALKENES WITH TWO HETEROATOM SUBSTITUENTS (Continued)



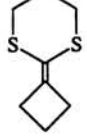


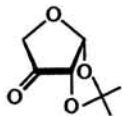



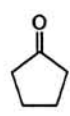
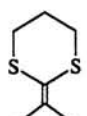
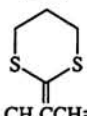
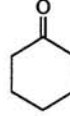
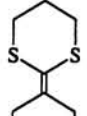
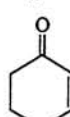
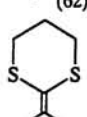
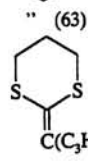
Silane						Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ²	R ³				
						<i>i</i> -C ₃ H ₇ CHO	"	 (69)	303, 304
						"	<i>n</i> -C ₄ H ₉ Li, THF, 0° <i>n</i> -C ₄ H ₉ Li, THF, -60°	 " (44)  (81)	239 308
						"	<i>n</i> -C ₄ H ₉ Li, THF, 0°	 (25)	239
						"	"	 (80)	239
						CH ₃ CH=C(CH ₃)-CHO	"	"	"
						"	<i>n</i> -C ₄ H ₉ Li, THF, -60°	 " (66) ^d	308
						<i>n</i> -C ₃ H ₇ COCH ₃	"	 CH ₃ CC ₃ H ₇ - <i>n</i>	308
							"	 (60)	308, 314
						(CH ₃) ₂ C=CHCO-CH ₃	"	 (69)	308
							"	 CH ₃ CCH=C(CH ₃) ₂ (80-92)	308, 314
						"	<i>n</i> -C ₄ H ₉ Li, THF, 0°	" (62)	239
							"	 (40)	239
						"	<i>n</i> -C ₄ H ₉ Li, THF, -60°	" (63)	308, 314
						(<i>n</i> -C ₃ H ₇) ₂ CO	"	 (80)	308

TABLE XVIII. FORMATION OF ALKENES WITH TWO HETEROATOM SUBSTITUENTS (Continued)

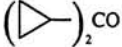
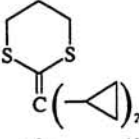
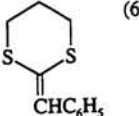
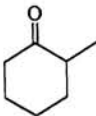
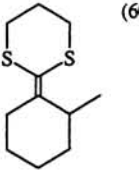
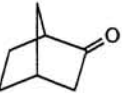
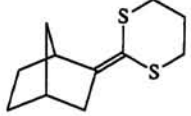
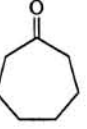
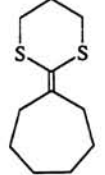
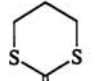
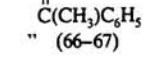
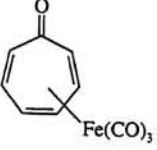
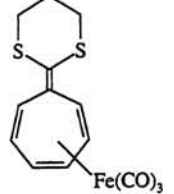
Silane						Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ²	R ³				
							<i>n</i> -C ₄ H ₉ Li, THF, 0°	 (68)	239
						C ₆ H ₅ CHO	<i>n</i> -C ₄ H ₉ Li, THF, -60°	 (68-95)	303, 304, 308, 314
								 (60-61)	308, 314
							<i>n</i> -C ₄ H ₉ Li, THF, 0°	 (64)	239
							<i>n</i> -C ₄ H ₉ Li, THF, -60°	 (80)	308
						C ₆ H ₅ COCH ₃	"	 (87)	308
						"	<i>n</i> -C ₄ H ₉ Li, THF, 0°	 (66-67)	303, 304
							—	 (40)	463

TABLE XVIII. FORMATION OF ALKENES WITH TWO HETEROATOM SUBSTITUENTS (Continued)


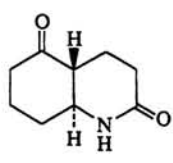
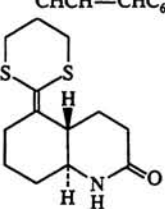
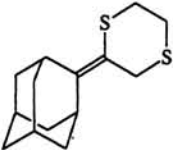
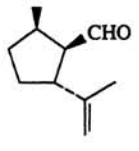
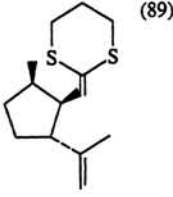
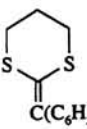
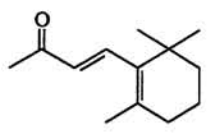
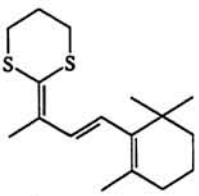
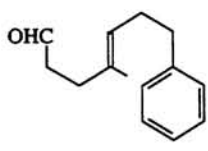
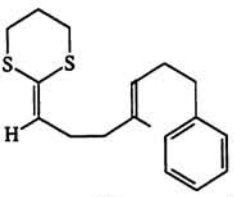
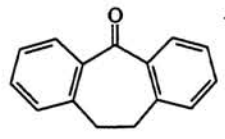
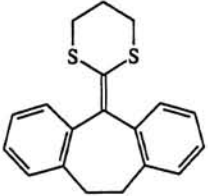
Silane						Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ²	R ³				
						C ₆ H ₅ CH=CHCHO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	 (66-70)	239, 303, 304
							"	 (83)	464
						Adamantanone	"	 (95)	239
							"	 (89)	309
						(C ₆ H ₅) ₂ CO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	 (75-78)	239, 303, 304
						"	<i>n</i> -C ₄ H ₉ Li, THF, -60°	" (87)	308, 314
							"	 (78)	308
							"	 (79)	310
							"	 (70)	463

TABLE XVIII. FORMATION OF ALKENES WITH TWO HETEROATOM SUBSTITUENTS (Continued)

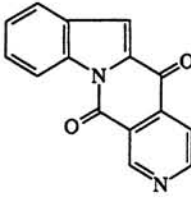
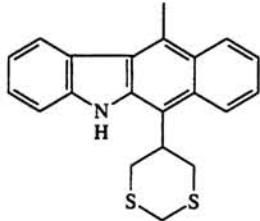
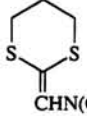
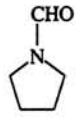
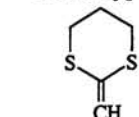
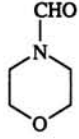
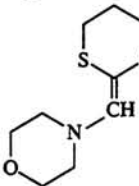

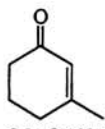
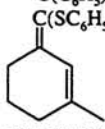
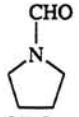
Silane						Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ²	R ³				
							1. <i>n</i> -C ₄ H ₉ Li 2. CH ₃ Li 3. NaBH ₄	 (25)	312
						(CH ₃) ₂ NCHO	<i>n</i> -C ₄ H ₉ Li, THF	 (45)	304
							<i>n</i> -C ₄ H ₉ Li, THF, -60°	 (82)	308, 314
							"	 (59)	308, 314
S	S	CH ₃	-CH ₂ SCH ₂		H	(C ₆ H ₅) ₂ CO	"	 (42)	308
S	S	CH ₃	C ₆ H ₅	C ₆ H ₅	H		<i>n</i> -C ₄ H ₉ Li, THF, 0°	 (48)	242
						C ₆ H ₅ CH(CH ₃)CHO	<i>n</i> -C ₄ H ₉ Li, THF, -60°	C ₆ H ₅ CH(CH ₃)CH=C(SC ₆ H ₅) ₂	308, 314
							"	HC=C(SC ₆ H ₅) ₂ (30)	308, 314
S	S	CH ₃	C ₆ H ₅	C ₆ H ₅	SC ₆ H ₅	CH ₂ O	LiC ₁₀ H ₈ , THF, -78°	CH ₂ =C(SC ₆ H ₅) ₂ (80)	241
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(SC ₆ H ₅) ₂ (78)	241
						(C ₆ H ₅) ₂ CO	"	(C ₆ H ₅) ₂ C=C(SC ₆ H ₅) ₂ (49)	241
S	Si	CH ₃	CH ₃	(CH ₃) ₃	H	CH ₂ O	<i>n</i> -C ₄ H ₉ Li, THF, -60°	CH ₂ =C(SCH ₃)Si(CH ₃) ₃ (79)	313
						CH ₃ CHO	"	CH ₃ CH=C(SCH ₃)Si(CH ₃) ₃ (53)	313
						<i>n</i> -C ₆ H ₁₁ CHO	"	<i>n</i> -C ₆ H ₁₁ CH=C(SCH ₃)Si(CH ₃) ₃ (71)	313
						CH ₂ O	"	CH ₂ =C(SC ₆ H ₅)Si(CH ₃) ₃ (84)	313
S	Si	CH ₃	C ₆ H ₅	(CH ₃) ₃	H	THPO(CH ₂) ₂ CHO	<i>n</i> -C ₄ H ₉ Li, THF, -78°	THPO(CH ₂) ₂ CH=C(SC ₆ H ₅)Si(CH ₃) ₃ (54)	465
						(<i>E</i>)-CH ₃ CH=CH-CHO	<i>n</i> -C ₄ H ₉ Li, THF, 0°	(<i>E</i>)-CH ₃ CH=CHCH=C(SC ₆ H ₅)Si(CH ₃) ₃ (14)	242
						<i>n</i> -C ₃ H ₁₁ CHO	<i>n</i> -C ₄ H ₉ Li, THF, -60°	<i>n</i> -C ₃ H ₁₁ CH=C(SC ₆ H ₅)Si(CH ₃) ₃ (70) ^c	313
						(C ₂ H ₅) ₂ CHCHO	"	(C ₂ H ₅) ₂ CHCH=C(SC ₆ H ₅)Si(CH ₃) ₃ (86)	313
						(CH ₃) ₂ C=CH-COCH ₃	<i>n</i> -C ₄ H ₉ Li, THF, 0°	(CH ₃) ₂ C=CHC(CH ₃)=C(SC ₆ H ₅)Si(CH ₃) ₃ (28)	242

TABLE XVIII. FORMATION OF ALKENES WITH TWO HETEROATOM SUBSTITUENTS (Continued)

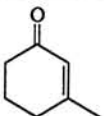
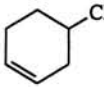
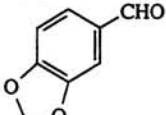
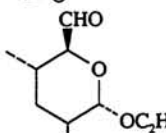
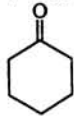
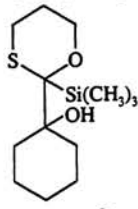
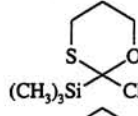
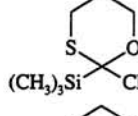
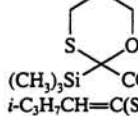
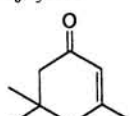

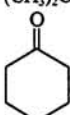

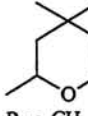
Silane						Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ²	R ³				
							"	$C(SC_6H_5)Si(CH_3)_3$ (22)	242
							$n-C_4H_9Li$, THF, -60°	$CH=C(SC_6H_5)Si(CH_3)_3$ (85)	313
						C_6H_5CHO	"	$C_6H_5CH=C(SC_6H_5)Si(CH_3)_3$ (76) ^c	313
							"	$CH=C(SC_6H_5)Si(CH_3)_3$ (74) ^e	313
							1. $n-C_4H_9Li$, THF 2. MCPBA	$HC=C(SO_2C_6H_5)Si(CH_3)_3$ (60)	317
S	Si	CH ₃	C ₆ H ₅	(CH ₃) ₃	SC ₆ H ₅	CH ₂ O	LiC ₁₀ H ₈ , THF, -78°	CH ₂ =C(SC ₆ H ₅)Si(CH ₃) ₃ (80)	241
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(SC ₆ H ₅)Si(CH ₃) ₃ (78)	241
						(C ₆ H ₅) ₂ CO	"	(C ₆ H ₅) ₂ C=C(SC ₆ H ₅)Si(CH ₃) ₃ (49)	241
S	Sn	CH ₃	CH ₃	(CH ₃) ₃	H	CH ₂ O	LDA, THF, HMPA, -78°	CH ₂ =C[Sn(CH ₃) ₃]SCH ₃ (33)	313
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C[Sn(CH ₃) ₃]SCH ₃ (60) $E:Z = 1:2$	313
						CH ₂ O	"	CH ₂ =C[Sn(CH ₃) ₃]SC ₆ H ₅ (71)	313
						$n-C_3H_7CHO$	"	$n-C_3H_7CH=C[Sn(CH_3)_3]SC_6H_5$ (74)	313
						$n-C_5H_{11}CHO$	"	$n-C_5H_{11}CH=C[Sn(CH_3)_3]SC_6H_5$ (74)	313
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C[Sn(CH ₃) ₃]SC ₆ H ₅ (82)	313
						(C ₆ H ₅) ₂ CO	"	(C ₆ H ₅) ₂ C=C[Sn(CH ₃) ₃]SC ₆ H ₅ (60)	313
S	Sn	CH ₃	C ₆ H ₅	($n-C_4H_9$) ₃	H	C ₆ H ₅ CHO	KDA, THF, -78°	C ₆ H ₅ CH=C[Sn(C ₄ H ₉) ₃]SC ₆ H ₅ (72)	260
						(C ₆ H ₅) ₂ CO	"	(C ₆ H ₅) ₂ C=C[Sn(C ₄ H ₉) ₃]SC ₆ H ₅ (46)	260
S	O	CH ₃	-(CH ₂) ₅ -		H		$s-C_4H_9Li$, THF, -78°		319
						C ₆ H ₅ CHO	"		(75) ^f 319
						C ₆ H ₅ CH=CHCHO	"		(76) ^f 319
						(C ₆ H ₅) ₂ CO	"		(46) ^f 319
S	O	CH ₃	C ₆ H ₅	CH ₃	H	$i-C_3H_7CHO$	$s-C_4H_9Li$, TMEDA, THF, -78°	$i-C_3H_7CH=C(SC_6H_5)OCH_3$ (96)	321
						(E)-CH ₃ CH=CH-CHO	"	(E)-CH ₃ CH=CHCH=C(SC ₆ H ₅)OCH ₃ (94)	321

TABLE XVIII. FORMATION OF ALKENES WITH TWO HETEROATOM SUBSTITUENTS (Continued)

Silane						Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ²	R ³				
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(SC ₆ H ₅)OCH ₃ (100)	321
							"	C ₆ H ₅ SCOCH ₃ (87)	321
							"	C ₆ H ₅ SCOCH ₃ (93)	321
						C ₄ H ₉ - <i>t</i> (<i>E</i>)-C ₆ H ₅ CH=CH-CHO	"	C ₄ H ₉ - <i>t</i> (<i>E</i>)-C ₆ H ₅ CH=CHCH=C(SC ₆ H ₅)OCH ₃ (100)	321
SO ₂	O	CH ₃	<i>p</i> -ClC ₆ H ₄	CH ₃	H	CH ₃ CHO	<i>n</i> -C ₄ H ₉ Li, THF, -70°	CH ₃ CH=C(OCH ₃)SO ₂ C ₆ H ₄ Cl- <i>p</i> (96)	322
						(CH ₃) ₂ CO	"	(CH ₃) ₂ C=C(OCH ₃)SO ₂ C ₆ H ₄ Cl- <i>p</i> (88)	322
							"	CH ₃ OCSO ₂ C ₆ H ₄ Cl- <i>p</i> (42)	322
						<i>p</i> -ClC ₆ H ₄ CHO	"	<i>p</i> -ClC ₆ H ₄ CH=C(OCH ₃)SO ₂ C ₆ H ₄ Cl- <i>p</i> (88)	322
						HCO ₂ CH ₃	"	CH ₃ OCH=C(OCH ₃)SO ₂ C ₆ H ₄ Cl- <i>p</i> (71)	322
Se	Se	CH ₃	C ₆ H ₅	C ₆ H ₅	H	CH ₂ O	LDA, THF, -78°	CH ₂ =C(SeC ₆ H ₅) ₂ (-) ^f	313
						C ₂ H ₅ CHO	"	C ₂ H ₅ CH=C(SeC ₆ H ₅) ₂ (-) ^f	313
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C(SeC ₆ H ₅) ₂ (85)	313
Si	Si	CH ₃	(CH ₃) ₃	(CH ₃) ₃	H	CH ₂ O	CH ₃ Li, THF	CH ₂ =C[Si(CH ₃) ₃] ₂ (70)	259, 313
						CH ₃ CHO	"	CH ₃ CH=C[Si(CH ₃) ₃] ₂ (22)	313
						<i>n</i> -C ₃ H ₇ CHO	"	<i>n</i> -C ₃ H ₇ CH=C[Si(CH ₃) ₃] ₂ (43)	313
						<i>t</i> -C ₄ H ₉ CHO	"	<i>t</i> -C ₄ H ₉ CH=C[Si(CH ₃) ₃] ₂ (73-80)	313, 325
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C[Si(CH ₃) ₃] ₂ (71-72)	313, 325
						(<i>E</i>)-C ₆ H ₅ CH=CH-CHO	"	(<i>E</i>)-C ₆ H ₅ CH=CHCH=C[Si(CH ₃) ₃] ₂ (50-53)	313, 325
						(C ₆ H ₅) ₂ CO	"	(C ₆ H ₅) ₂ C=C[Si(CH ₃) ₃] ₂ (25)	313
Si	Si	CH ₃	(CH ₃) ₃	(CH ₃) ₃	SC ₆ H ₅	CH ₂ O	LiC ₁₀ H ₈ , THF, -78°	CH ₂ =C[Si(CH ₃) ₃] ₂ (73)	241
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=C[Si(CH ₃) ₃] ₂ (68)	241
						(C ₆ H ₅) ₂ CO	"	(C ₆ H ₅) ₂ C=C[Si(CH ₃) ₃] ₂ (21)	241
Si	Br	CH ₃	(CH ₃) ₃	—	Br	CH ₃ CHO	<i>n</i> -C ₄ H ₉ Li, THF, C ₆ H ₁₄ , -115°	CH ₃ CH=CBrSi(CH ₃) ₃ (78) + E:Z = 1:1 (CH ₃) ₃ Si 	326
						<i>i</i> -C ₃ H ₇ CHO	"	<i>i</i> -C ₃ H ₇ CH=CBrSi(CH ₃) ₃ (52)	326
						<i>t</i> -C ₄ H ₉ CHO	"	<i>t</i> -C ₄ H ₉ CH=CBrSi(CH ₃) ₃ (64) + E:Z = 1:1.8	326
						C ₆ H ₅ CHO	"	<i>t</i> -C ₄ H ₉ CH=C[Si(CH ₃) ₃] ₂ (9)	326
						<i>t</i> -C ₄ H ₉ CH=CH-CHO	"	C ₆ H ₅ CH=CBrSi(CH ₃) ₃ (68)	326
						CH ₃ CHO	"	<i>t</i> -C ₄ H ₉ CH=CHCH=CBrSi(CH ₃) ₃ (73)	326
						CH ₃ CHO	<i>n</i> -C ₄ H ₉ Li, THF, -78°	 R = CH ₃ E:Z = 76:24	(-) 222
						C ₂ H ₅ CHO	"	R = C ₂ H ₅ E:Z = 86:14	(-) 222

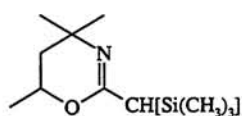
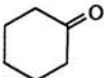




TABLE XVIII. FORMATION OF ALKENES WITH TWO HETEROATOM SUBSTITUENTS (Continued)

		Silane				Carbonyl Compound	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
X	Y	R	R ¹	R ²	R ³				
						<i>i</i> -C ₃ H ₇ CHO	"	R = <i>i</i> -C ₃ H ₇ <i>E:Z</i> = 93:7	(—) 222
						C ₆ H ₅ CHO	"	R = C ₆ H ₅ <i>E:Z</i> = 90:10	(—) 222
C ₃		TMSCCl ₂ CH=CH ₂					<i>n</i> -C ₄ H ₉ Li, THF, -90°	 (27)	274
								 (57)	
						<i>n</i> -C ₆ H ₁₃ CHO	"	<i>n</i> -C ₆ H ₁₃ CH=CClCH=CH ₂ (60) + <i>n</i> -C ₆ H ₁₃ CHOHCH ₂ CH=CClSi(CH ₃) ₃ (28)	274
						C ₆ H ₅ CHO	"	C ₆ H ₅ CH=CClCH=CH ₂ (26) + C ₆ H ₅ CHOHCH ₂ CH=CClSi(CH ₃) ₃ (67)	274
						C ₆ H ₅ COCH ₃	"	C ₆ H ₅ C(CH ₃)=CClCH=CH ₂ (43) + C ₆ H ₅ C(CH ₃)OHCH ₂ CH=CClSi(CH ₃) ₃ (8) + C ₆ H ₅ C(CH ₃)[OSi(CH ₃) ₃]CH ₂ - CH=CClSi(CH ₃) ₃ (13) + C ₆ H ₅ C[OSi(CH ₃) ₃]=CH ₂ (10) + (C ₆ H ₅) ₂ C(CH ₃)OSi(CH ₃) ₃ (19)	274

^a Only the *E* isomer is isolated.

^b The yield is determined by GC analysis.

^c The product is obtained as a mixture of isomers.

^d The yield is determined by NMR.

^e Two equivalents of the carbanion are used.

^f The product is obtained as a mixture of diastereoisomers.

^g The product is not isolated.

TABLE XIX. RELATED REACTIONS WITH OTHER ELECTROPHILES

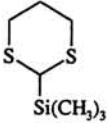
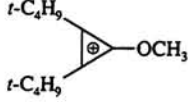
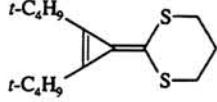
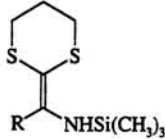
Silane	Electrophile	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C₀				
C ₆ H ₅ NHSi(CH ₃) ₃	SO ₂	1. <i>n</i> -C ₄ H ₉ Li, THF, 0°	C ₆ H ₅ N=S=O (74)	227
<i>p</i> -CH ₃ C ₆ H ₄ NHSi(CH ₃) ₃	"	"	<i>p</i> -CH ₃ C ₆ H ₄ N=S=O (90)	227
<i>p</i> -ClC ₆ H ₄ NHSi(CH ₃) ₃	"	"	<i>p</i> -ClC ₆ H ₄ N=S=O (73)	227
<i>m</i> -CH ₃ OC ₆ H ₄ NHSi(CH ₃) ₃	"	"	<i>m</i> -CH ₃ OC ₆ H ₄ N=S=O (64)	227
<i>o,o</i> -(CH ₃) ₂ C ₆ H ₃ NHSi(CH ₃) ₃	"	"	<i>o,o</i> -(CH ₃) ₂ C ₆ H ₃ N=S=O (85)	227
<i>o,o,p</i> -(CH ₃) ₃ C ₆ H ₂ NHSi(CH ₃) ₃	"	"	<i>o,o,p</i> -(CH ₃) ₃ C ₆ H ₂ N=S=O (85)	227
<i>o,o</i> -(<i>i</i> -C ₃ H ₇) ₂ C ₆ H ₃ NHSi(CH ₃) ₃	"	"	<i>o,o</i> -(<i>i</i> -C ₃ H ₇) ₂ C ₆ H ₃ NHSi(CH ₃) ₃ (79)	227
<i>o,p</i> -(<i>t</i> -C ₄ H ₉) ₂ C ₆ H ₃ NHSi(CH ₃) ₃	"	"	<i>o,p</i> -(<i>t</i> -C ₄ H ₉) ₂ C ₆ H ₃ N=S=O (80)	227
C ₆ H ₁₁ NHSi(CH ₃) ₃	"	"	C ₆ H ₁₁ N=S=O (62)	227
[(CH ₃) ₃ Si] ₂ NH	C ₂ H ₅ NSO	<i>n</i> -C ₄ H ₉ Li, C ₆ H ₁₄	C ₂ H ₅ N=S=NSi(CH ₃) ₃ (9)	356
	<i>t</i> -C ₄ H ₉ NSO	"	<i>t</i> -C ₄ H ₉ N=S=NSi(CH ₃) ₃ (65)	356
	C ₆ H ₅ NSO	"	C ₆ H ₅ N=S=NSi(CH ₃) ₃ (26)	356
C₁				
	<i>t</i> -C ₄ H ₉ 	1. <i>n</i> -C ₄ H ₉ Li, THF 2. CH ₃ CN, heat	 (54)	358
	C ₆ H ₅ CN	1. <i>n</i> -C ₄ H ₉ Li		354
	<i>p</i> -CH ₃ C ₆ H ₄ CN	2. H ₃ O ⁺	R = C ₆ H ₅ (67)	354
	4-Cyanopyridine	"	R = <i>p</i> -CH ₃ C ₆ H ₄ (78)	354
		"	R = 4-pyridyl (61)	354

TABLE XIX. RELATED REACTIONS WITH OTHER ELECTROPHILES (Continued)

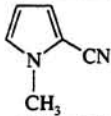
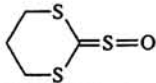
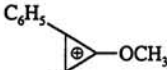
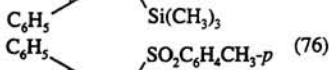
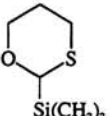
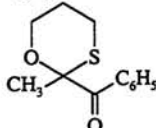
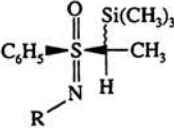
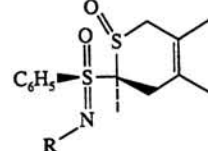
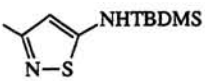
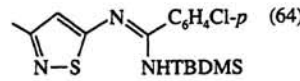
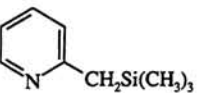
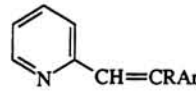
Silane	Electrophile	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.		
		"	R = <i>N</i> -methyl-5-pyrrolyl (96)			
	<i>o</i> -Cyanothiophenol	"	R = 2-thiophenyl (27)	354		
	<i>p</i> -BrC ₆ H ₄ CN	"	R = <i>p</i> -BrC ₆ H ₄ (48)	354		
	<i>t</i> -C ₄ H ₉ CN	"		354		
	SO ₂	<i>n</i> -C ₄ H ₉ Li, THF, -78°	 (80)	344		
(C ₆ H ₅ S) ₂ CHSi(CH ₃) ₃	"	"	(C ₆ H ₅ S) ₂ C=S=O (80)	344		
(C ₆ H ₅ SO ₂ CH[Si(CH ₃) ₃]) ₂		1. <i>n</i> -C ₄ H ₉ Li, THF 2. CH ₃ CN, heat	C ₆ H ₅ SO ₂ C ₆ H ₅ (70)	358		
<i>p</i> -CH ₃ C ₆ H ₄ SO ₂ CH[Si(CH ₃) ₃] ₂	"	"	 (76)	358		
	C ₆ H ₅ CN	1. C ₆ H ₅ Li, THF, -78° 2. CH ₃ I 3. H ₃ O ⁺	 (45)	353		
C ₂		SO ₂	1. <i>n</i> -C ₄ H ₉ Li, THF, -78° 2. CH ₂ =C(CH ₃)C(CH ₃)=CH ₂	 (40) R = <i>p</i> -CH ₃ C ₆ H ₄ (60)	344	
C ₃ ^a	CH ₂ =C(SO ₂ C ₆ H ₅)Si(CH ₃) ₃	"	CH ₃ Li, TMEDA, THF, -78°	CH ₃ CH ₂ C(=S=O)SO ₂ C ₆ H ₅ (74) ^b	128	
C ₄		<i>p</i> -ClC ₆ H ₄ CN	<i>n</i> -C ₄ H ₉ Li, THF	 (64)	355	
C ₆		R ¹ N=CRAr	1. LDA, THF, -75° 2. NH ₄ Cl, H ₂ O			
		R	R	Ar		
		C ₆ H ₅	H	C ₆ H ₅	(84) <i>E</i> : <i>Z</i> = 100:0	346
		<i>p</i> -ClC ₆ H ₄	H	C ₆ H ₅	(32) <i>E</i> : <i>Z</i> = 100:0	346
		C ₆ H ₅	H	2-pyridyl	(54) <i>E</i> : <i>Z</i> = 100:0	346
		C ₆ H ₅	H	C ₆ H ₅ CH=CH	(68) ^c	346
		CH ₃	H	C ₆ H ₅	(10) ^d <i>E</i> : <i>Z</i> = 99.6:0.4	
		<i>t</i> -C ₄ H ₉	H	C ₆ H ₅	(5) ^d	346
		C ₆ H ₅	CH ₃	C ₆ H ₅	(10) ^d <i>E</i> : <i>Z</i> = 87.5:12.5	346

TABLE XIX. RELATED REACTIONS WITH OTHER ELECTROPHILES (Continued)

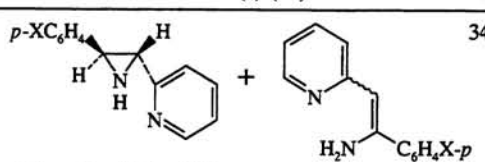
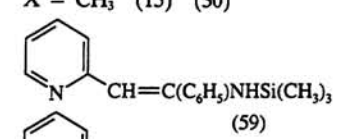
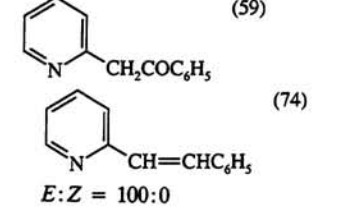
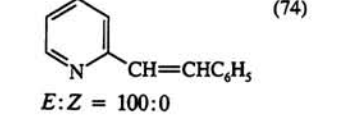
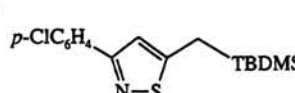
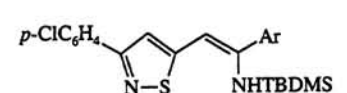
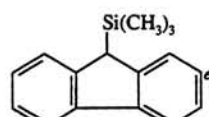
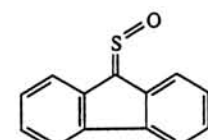
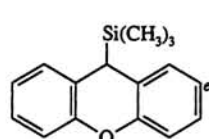
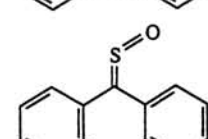
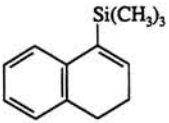
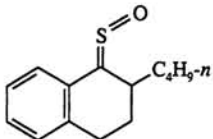
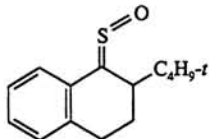
Silane	Electrophile	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$p\text{-XC}_6\text{H}_4\text{CH=NOCH}_3$	LDA, THF, -90°		347
	X = Cl	"	X = Cl (12) (30)	347
	X = H	"	X = H (38) (11)	347
	X = CH ₃	"	X = CH ₃ (15) (30)	347
	C ₆ H ₅ CN	1. LDA, THF, -75° 2. H ₂ O	(15) +  (59)	352
	C ₆ H ₅ CH=NN(CH ₃)C ₆ H ₅	1. LDA, 18-crown-6, THF, 0° 2. Heat	 (74)  (75) <i>E:Z</i> = 100:0	348
C ₆ ^a	CH ₂ =C(SC ₆ H ₅)Si(CH ₃) ₃	<i>n</i> -C ₄ H ₉ Li, TMEDA, THF, -78°	<i>n</i> -C ₄ H ₉ CH ₂ C(=S=O)SC ₆ H ₅ (15)	128
	"	<i>t</i> -C ₄ H ₉ Li, TMEDA, THF, -78°	<i>t</i> -C ₄ H ₉ CH ₂ C(=S=O)SC ₆ H ₅ (73)	128
	CH ₂ =C(SO ₂ C ₆ H ₅)Si(CH ₃) ₃	<i>n</i> -C ₄ H ₉ Li, TMEDA, THF, -78°	<i>n</i> -C ₄ H ₉ CH ₂ C(=S=O)SO ₂ C ₆ H ₅ (50)	128
	"	<i>t</i> -C ₄ H ₉ Li, TMEDA, THF, -78°	<i>t</i> -C ₄ H ₉ CH ₂ C(=S=O)SO ₂ C ₆ H ₅ (51)	128
C ₇	C ₆ H ₅ CH(SC ₆ H ₅)Si(CH ₃) ₃	1. <i>n</i> -C ₄ H ₉ Li, THF, -78° 2. -20°	C ₆ H ₅ C(=S=O)SC ₆ H ₅ (60) <i>E:Z</i> = 34:26	344
	C ₆ H ₅ CH(SO ₂ C ₆ H ₅)Si(CH ₃) ₃	"	C ₆ H ₅ C(=S=O)SO ₂ C ₆ H ₅ (70) <i>E:Z</i> = 100:0	344
	C ₆ H ₅ CHCNSi(CH ₃) ₃	"	C ₆ H ₅ C(=S=O)CN (41) ^c	344
C ₈ ^a	CH ₂ =C(SO ₂ C ₆ H ₅)Si(CH ₃) ₃	C ₆ H ₅ Li, TMEDA, THF, -78°	C ₆ H ₅ CH ₂ C(=S=O)SO ₂ C ₆ H ₅ (72)	344
C ₁₀		ArCN Ar = <i>p</i> -ClC ₆ H ₄ Ar = <i>m,m</i> -Cl ₂ C ₆ H ₃ Ar = <i>p</i> -CH ₃ C ₆ H ₄	 Ar = <i>p</i> -ClC ₆ H ₄ (61) Ar = <i>m,m</i> -Cl ₂ C ₆ H ₃ (50) Ar = <i>p</i> -CH ₃ C ₆ H ₄ (45)	355 355 355
C ₁₂ ^a	CH ₂ =C(C ₆ H ₅)Si(CH ₃) ₃	<i>n</i> -C ₄ H ₉ Li, TMEDA, THF, -78°	<i>n</i> -C ₄ H ₉ CH ₂ COC ₆ H ₅ (42)	128
	"	<i>t</i> -C ₄ H ₉ Li, TMEDA, THF, -78°	<i>t</i> -C ₄ H ₉ CH ₂ C(=S=O)C ₆ H ₅ (29) + <i>t</i> -C ₄ H ₉ CH ₂ COC ₆ H ₅ (17)	128
C ₁₃		1. <i>n</i> -C ₄ H ₉ Li, THF, -78° 2. -20°	 (80)	355
		"	 (80)	355

TABLE XIX. RELATED REACTIONS WITH OTHER ELECTROPHILES (Continued)

Silane	Electrophile	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}^a 	"	$n-C_4H_9Li$, TMEDA, THF, -78°	 (30)	128
	"	$t-C_4H_9Li$, TMEDA, THF, -78°	 (33)	128

^a This compound is derived from the α -silylcarbanion through addition of the alkyllithium to the alkene.

^b The yield is determined by NMR.

^c The isomer ratio is not given.

^d The yield is determined by GC.

^e The silane is prepared in situ.

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Errata for Paquette: ORGANIC REACTIONS, Volume 38

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The following references were inadvertently omitted and should appear at the end of the reference list on page 223.

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