

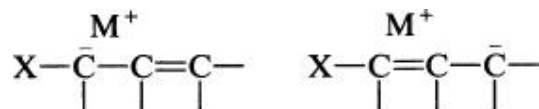
# Allylic and Benzylic Carbanions Substituted by Heteroatoms

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## 1. Introduction

This review covers carbanions of the following structure



in which X is a heteroatom and the double bond may be part of a conjugated system. Propargylic and allenic systems are also included. The cation  $\text{M}^+$  is an alkaline or alkaline-earth element; transition metals are excluded. The chapter by Gilman and Morton in 1954 (1) was restricted to lithium derivatives. Reviews covering part of the subject include those on organometallic compounds, (2-4) on reagents for nucleophilic acylation, (5) on olefin synthesis with P(O)-activated reagents, (6, 7) on the formation and reactions of carbanions derived from allylic sulfoxides, (8) dithianes, (9) nitrosoamines, (10) thioethers and ethers, (11, 12) selenium compounds, (13) on base-catalyzed isomerization, (14) and on rearrangements of carbanions. (15, 16)

### 1.1. Nature of the Heteroatom

Allylic and benzylic carbanions adjacent to the following *heteroatoms* have been described:

1. *Boron*, as in an organoborane with a vinylic substituent. (17)
2. *Nitrogen*, as in an amine, (18) amine *N*-oxide, (18a) enamine, (19) ynamine, (20) isonitrile, (21) thioisonitrile, (22) nitrosoamine, (23) iminodithiocarbonate diester, (24) amide, (25) bis(dialkylamino)phosphoramidate, (26) dialkylaminoalkoxyphosphoramidate, (27) bis(alkoxy)phosphoramidate, (28) sulfonamide, (29) and nitro compound. (29a)
3. *Oxygen*, as in an alkyl, aryl, tetrahydropyranyl, (30) trialkylsilyl ether, (31, 32) cyanohydrin ether, (33) ketal, (34) hemithioketal, (35) and bisdimethylamido- and dialkyl phosphate ester. (36)
4. *Silicon*, as in a silane. (37)
5. *Phosphorus*, as in a phosphine oxide, (38) phosphine sulfide, (39) phosphinate, (40) phosphinamide, (39) thiophosphinate, (39) phosphonate, (41) and phosphonamide. (42)

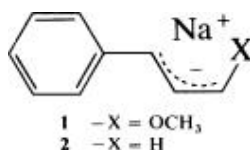
6. *Sulfur*, as in a thiol, (43) alkyl and aryl thioether, (44) dithioester, (45) thiothiazoline, (46) trialkyl silyl thioether, (47) *N,N*-dimethyldithiocarbamate, (48) dithioacetal, (49) diphenylphosphinodithioate and diphenylphosphinothioate, (50) sulfoxide (51) and sulfoximine, (52) sulfone (53) and sulfoximine, (52) sulfonic ester, (54) dialkylsulfonamide, (55) and thioketone. (56)
7. *Chlorine*, as in a benzyl or allyl tri-, di-, and monochloride. (57)
8. *Selenium*, as in an arylselenide (58) and arylselenoxide. (59)
9. *Bromine*, as in a monobromide or a dibromide. (60)
10. *Tellurium*, as in a telluride. (61)

The basicity and structures of these anions are considered first. This discussion is followed by sections on methods of generation of carbanions, reactions occurring during preparation, decomposition, and rearrangements of carbanions, reactions with electrophiles, regioselectivity and stereochemical aspects of the reactions, transformations of the reaction products, and some applications of these carbanions in synthesis.

## 2. Carbanions

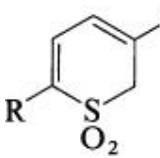
### 2.1. Basicity

Are heterosubstituted carbanions more or less basic than the parent carbanion in which the heteroatom is replaced by a hydrogen? With some very acidifying substituents such as sulfone, sulfoxide, or phosphonyl, the answer is yes, but with others the answer is not so clear. Some experiments using an isotope-exchange method suggest that the oxygen in ethers renders the compound less acidic than the parent hydrocarbon. (62-64) Such results agree with nuclear magnetic resonance (nmr) measurements: the electron density determined by the chemical shift is higher at the *para* carbon in the carbanion **1** than at the *para* carbon of the unsubstituted anion **2**. (65)



Published  $pK_a$ 's are summarized in Table 1.

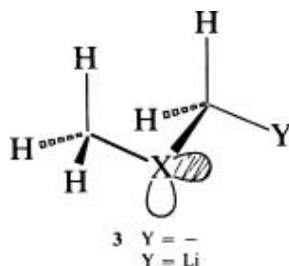
**Table 1. Acidity Constants**

Compound	$pK_a$	Method	Refs.
C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	30.8	Equilibrium, Potassium salt in Me <sub>2</sub> SO	67
C <sub>6</sub> H <sub>5</sub> SCH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	26.7	The same	67
(C <sub>6</sub> H <sub>5</sub> S) <sub>2</sub> CHC <sub>6</sub> H <sub>5</sub>	23.0	The same	67
1,3-Dithiane	31.2	Equilibrium, Cesium salt in cyclohexane	68
2-Phenyl-1,3-dithiane	28.2	The same	68
2- <i>p</i> -Biphenyl-1,3-dithiane	26.1	The same	68
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	22	Equilibrium, Potassium salt in Me <sub>2</sub> SO	69
[C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub>	23.5	The same	69
	10.79	Equilibrium in H <sub>2</sub> O	70
R = H	12.36	The same	70
R = CH <sub>3</sub>			
C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	20.3	Equilibrium,	66

		Potassium salt in Me <sub>2</sub> SO	
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PCH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	20.2	The same	66
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	23.4	The same	66
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>3</sub> Ar	21.7	Exchange in D <sub>2</sub> O	72

Recent experiments show that the kinetic acidities determined by the rate of base-catalyzed exchange are not always a good indication of the thermodynamic acidity. (66) Care should be taken so that internal return does not complicate the exchange kinetics. However, this is not the case for one sulfoxide. (73)

The acidifying effect of sulfur has been the subject of numerous speculations. The effect of the empty *d* orbital was an early explanation but at present this is less favored. In addition to the purely polar effect, some authors propose an electron-acceptor conjugation of the sulfur with the alpha carbanion. (74) Recent calculations agree with a polarizability effect. (75-77) *Ab initio* calculations on  $\text{CH}_3\text{CH}_2^-$ ,  $\text{HOCH}_2^-$ ,  $\text{CH}_3\text{OCH}_2^-$ ,  $\text{HSCH}_2^-$ ,  $\text{CH}_3\text{SCH}_2^-$ , and  $\text{CH}_3\text{SeCH}_2^-$  show that carbanion stabilization by the alpha heteroatom is subject to appreciable stereoelectronic effects. The "equatorial" type **3** is found to be the most stable. (78, 79) This explains some stereoselective reactions such as the equatorial reactivity of dithianes. (80, 81)

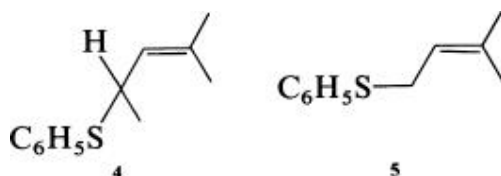


The  $pK_a$ 's of substituted 1,3-dithianes were determined by an equilibrium method as the cesium salts in cyclohexylamine. On the basis of substituent effects it was proposed that the anionic carbon is planar in the aryl-substituted dithiane anion. (68)

The effect of a thiophenyl group on the  $pK_a$  was measured by an equilibrium method in dimethyl sulfoxide. The introduction of this group increases the acidity from 4.9 to 11.5  $pK_a$  units and the cumulative effect of this group is

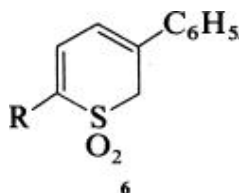
additive, which is contrary to the effect of the phenyl group. (66, 67) The diphenylphosphino group  $(C_6H_5)_2P$  - has about the same effect as the thiophenyl group. (66)

Experiments suggest that increased alkyl substitution decreases acidity. For instance, the thioether **4** is not metalated by *n*-butyllithium under conditions where the thioether **5** reacts. (82) This seems to favor an  $sp^3$ -hybridized carbanion in which the methyl group has an inductive effect unfavorable for carbanion formation. (83)



For protons alpha to a sulfone group the introduction of phenyl conjugation increases the acidity even more than for dithianes. Dimethyl sulfone has a  $pK_a$  of 28.5, dibenzyl sulfone 22, (69) and methyl phenyl sulfone 27.

Anomalously low  $pK_a$ 's were found for the cyclic sulfones **6**: R = H, 10.75 (H<sub>2</sub>O); R = CH<sub>3</sub>, 12.36 (H<sub>2</sub>O).



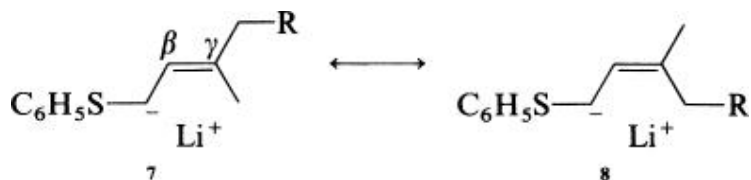
It was suggested that the anion has aromatic character. (70, 71)

The number of calculations on carbanions alpha to heteroatoms almost exceeds the number of  $pK_a$  determinations. However, further studies of structural effects are needed on the basicity of heterosubstituted carbanions.

## 2.2. Structures

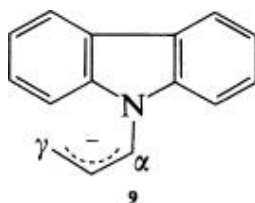
Interesting facts have emerged from the structural investigation of crystalline carbanions, e.g., benzyl lithium and indenyl lithium. (84-86) Similar studies have not been undertaken with heterosubstituted carbanions even though their stability is probably adequate. Such work could provide information on a number of important points including the chelation of the cation by the heteroatom, location of the cation relative to the conjugated system, and conformation in the reacting molecules.

Some details of the structures of heterosubstituted carbanions can be deduced from the stereochemistry of the reaction products (see Stereochemistry section, p. 40). The carbanions of thioethers **7** and **8** do not interconvert at  $-18^\circ$ . The lower limit of activation energy of 19.5 kcal/mol was

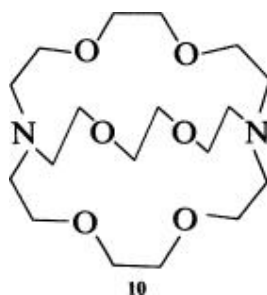


estimated for the rotation of the beta - gamma bond. (87) This value is higher than for comparable carbon systems (88) and it has been suggested that the rotation about the alpha - beta bond is slow in carbanions derived from propenyl and allyl phenyl ethers. (89)

The carbanion **9** was studied by nmr spectroscopy. The chain has the stereochemistry indicated in formula **9** and the chemical shifts suggest equal electron densities at the alpha and gamma carbon atoms. (90)



Dissociation and solvation of ion pairs of heterosubstituted carbanions have been little studied except for carbanions derived from thioethers and sulfoxides. Conductivity measurements at  $-78^\circ$  of the lithium carbanion derived from methyl benzyl sulfoxide at various concentrations show that in tetrahydrofuran and tetrahydrofuran-N,N,N',N'-tetramethylethylenediamine there are no free ions. However, after addition of cryptand[2.2.2] **10**,



triple ions and free ions appear to some extent. The slow appearance of

conductivity was attributed to a gradual dissociation. In contrast, the carbanion from benzyl phenyl thioether is present in tetrahydrofuran at  $-78^{\circ}$  in part as a free ion and the increase in conductivity is rapid after addition of cryptand[2.2.2]. Though more basic, the thioether carbanion is more dissociated than the sulfoxide carbanion. This is attributed to a strong interaction of the sulfoxide group with the lithium. These results are consistent with  $^{13}\text{C}$  and  $^1\text{H}$  nmr measurements. (91, 92)

The carbanion derived from benzyltrimethylsilane has been studied by  $^{13}\text{C}$  nmr spectroscopy. The corresponding lithium carbanion is a solvent-separated ion pair or a contact ion pair depending on the temperature, while the sodium carbanion is a contact ion pair. (92a) The classical spectroscopic study of the fluorenyl anion has been extended to C-9 sulfur substituted compounds  $\text{C}_6\text{H}_5\text{S}(\text{O})_n$  where  $n = 0, 1, 2$ . The solvent-separated ion pair for the thioether carbanion in tetrahydrofuran at  $20^{\circ}$  and the contact ion pair were found in 2-methyltetrahydrofuran even at low temperatures. The sulfone carbanion is both a contact ion pair and a solvent-separated ion pair according to  $^1\text{H}$  nmr measurements. (92b)

More developments should be expected in the areas of the basicity and the structure of heterosubstituted carbanions. It is important to determine how the presence of a heteroatom influences the structure of the carbanion. Through a better understanding of structural effects, it might be possible to improve the yield, the regioselectivity, and the stereoselectivity of these reactions.

### 3. Methods of Generation of Heterosubstituted

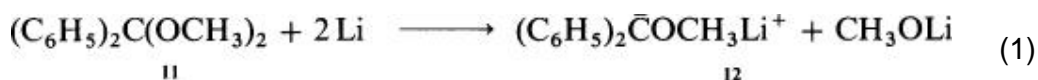
#### Carbanions

Heterosubstituted carbanions are prepared by the usual methods for generating carbanions. Side reactions caused by the heteroatom sometimes make it necessary to use more selective agents such as dialkylamides. It is possible to generate the heterosubstituted carbanions by special methods such as fragmentation or addition.

The methods of generating ions are presented in the following order: action of metals, metalations by reagents such as metal alkyls and aryls, amides, alkoxides, hydrides, *etc.*, transmetalation, halogen-metal interchange, addition, and fragmentation. Side reactions occurring during the preparation of carbanions are discussed. The chapter ends with a procedure for choosing a suitable metalating reagent.

#### 3.1. Action of Metal

The action of lithium on benzophenone dimethyl ketal **11** yields a carbanion **12** by cleavage of a carbon-oxygen bond (Eq. 1). (93, 94)



This method has not been used much for the preparation of heterosubstituted carbanions. However, an alternate procedure employs the cleavage of a phenylthio ether with a lithium arylide to generate the desired intermediate. 94a,b

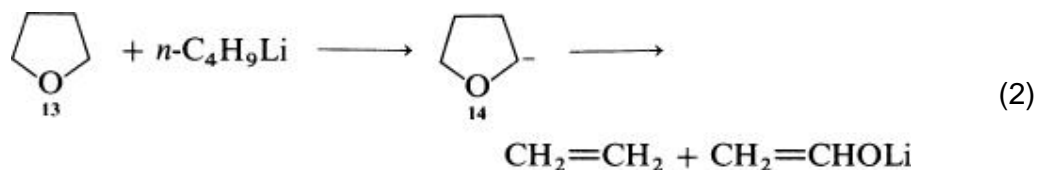
#### 3.2. Metalations

A proton alpha to the heteroatom in substituted allylic or benzylic systems can be removed with a more basic agent. A large variety of such agents are used, with *n*-butyllithium being the most common. The introduction of sterically hindered amides has extended the metalation procedure to compounds carrying substituents that react with organolithiums. Sodium and potassium hydride and corresponding alkoxides have been less frequently used. Possibly in many of the cases described in the tables, other bases and solvents would give similar results and yields might be improved by exploring other experimental conditions.

*n*-Butyllithium as the commercially available solution in a hydrocarbon is used in a stoichiometric amount with the compound to be metalated in solution in tetrahydrofuran. The temperature is usually below 0°, sometimes -78°. At



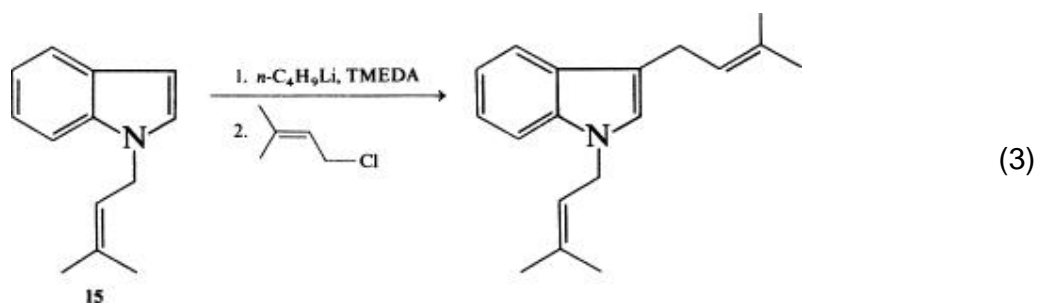
lower temperatures, tetrahydrofuran–diethyl ether mixtures can be used. At low temperature *n*-butyllithium has a low reactivity because of its polymeric nature. By addition of a chelating agent, usually N,N,N $\phi$ ,N $\phi$ -tetramethylethylenediamine (TMEDA), in molar amounts, the polymer is broken down. Decomposition of tetrahydrofuran **13** by *n*-butyllithium is not negligible at 20° (Eq. 2). (99)



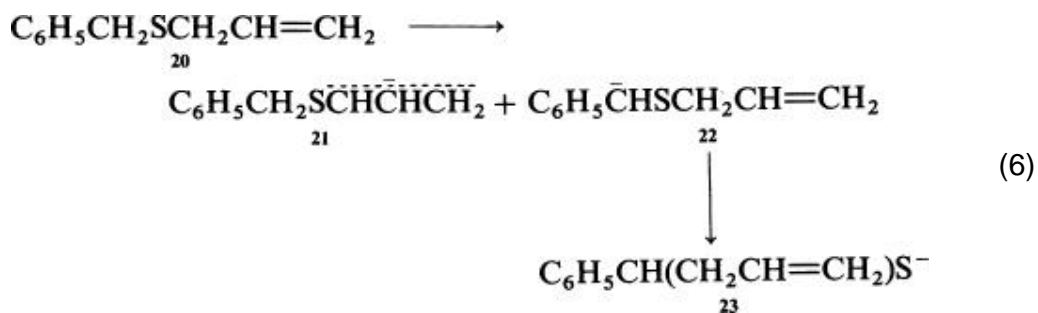
This decomposition can also be brought about by the newly generated carbanion **14**. If a temperature above 0° is needed to prepare the carbanion, the next step must be carried out without delay for a reasonable yield.

With allylic systems *n*-butyllithium is the most commonly used base. Its action is commented on only if side reactions occur or if special conditions must be used, such as addition of potassium *t*-butoxide or of hexamethylphosphoramide. Otherwise the reader is referred to the tables.

With N-prenylindole **15** and N-prenylcarbazole **16** the reaction of *n*-butyllithium is complex (Eqs. 3 and 4). With the former the enamine proton seems to be removed to some extent, and with the latter the allylic proton is

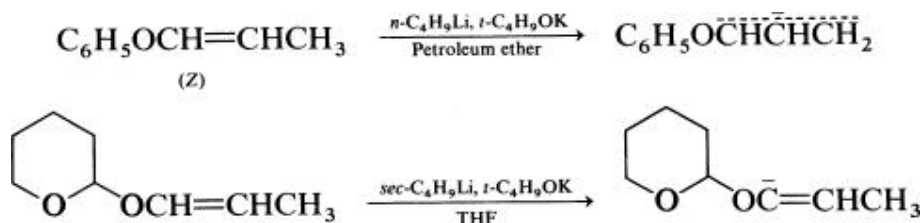




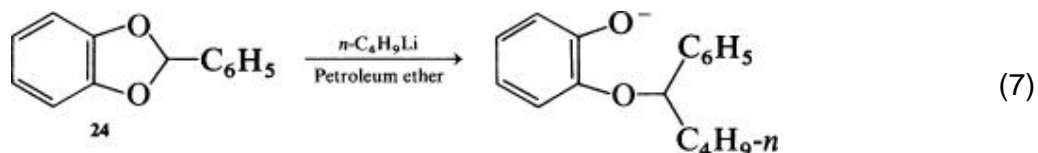


The metalation of 3-nitropropene to the dianion occurs cleanly with *n*-butyllithium in tetrahydrofuran in the presence of hexamethylphosphoramide at  $-80$  to  $-90^\circ$ . (29a)

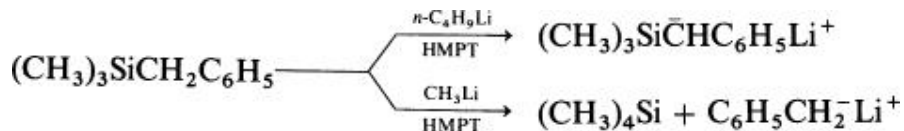
The reactivity of *n*-butyllithium can be enhanced by adding potassium *t*-butoxide. Allylmethylphenylamine does not react with *n*-butyllithium in tetrahydrofuran, but is metalated by *n*-butyl- or *t*-butyllithium in the presence of potassium *t*-butoxide in hexane. (89, 103) The allylic proton is removed in phenyl (*Z*)-propenyl ether by *n*-butyllithium–potassium *t*-butoxide in petroleum ether (103) and the vinylic proton is removed in the corresponding tetrahydropyranyl ether by *sec*-butyllithium–potassium *t*-butoxide in tetrahydrofuran. (105) Since two items, the solvent and the substituent, have been changed, it is not clear if both or only one factor is important for the change in regioselectivity.



Reaction of the acetal 24 with *n*-butyllithium proceeds by cleavage of the oxygen-carbon bond (Eq. 7). (106)



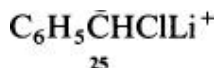
With silanes, *n*-butyllithium–hexamethylphosphoramide was used. In contrast, methylithium attacks at silicon. (107)



Allyltriphenylsilane in ether is metalated with *n*-butyllithium-*N,N,N',N'*-tetramethylethylenediamine. (108)

Ketene dithioketals are metalated by *n*-butyllithium in tetrahydrofuran in the presence of hexamethylphosphoramide (9, 109) and by sodium amide in hexamethylphosphoramide. (110)

The reaction of *n*-butyllithium with benzyl chloride is very sensitive to the solvent. In *n*-hexane, diethyl ether, and dioxane the reaction products are best explained by the formation of benzyllithium. However, in tetrahydrofuran carbanion **25** must be formed, leading to stilbene. (60, 111) This carbanion is best produced at  $-100^\circ$  in tetrahydrofuran, similar to the one derived from benzyldiene chloride. (112) With benzyl bromide attack occurs at the bromine atom. (60, 111)

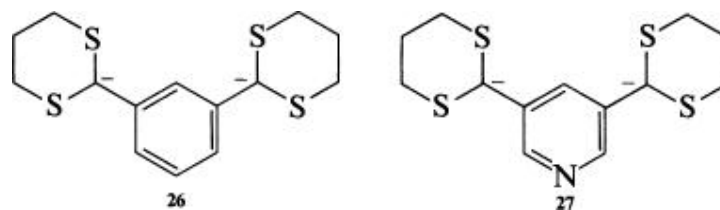


The action of a base on a vinylic system is more complex. In addition to the removal of the allylic proton, two other reactions may compete: addition of the base to the double bond and removal of the vinylic proton. Enamines are metalated at the allylic carbon by *n*-butyllithium in tetrahydrofuran-hexamethylphosphoramide (113) or by *t*-butyllithium, which has a higher reactivity than *n*-butyllithium. (103) Vinyl ethers, depending on the substituents at oxygen and on the base, give vinylic or allylic carbanions. With *n*-amylsodium in petroleum ether or *t*-butyllithium-*N,N,N',N'*-tetramethylethylenediamine in tetrahydrofuran, the vinylic proton is removed from 1-methoxy and 1-ethoxy-1-propene. (114-117)

Many dianions can be produced by the action of *n*-butyllithium. Benzyl and allyl thiols are metalated by *n*-butyllithium-*N,N,N',N'*-tetramethylethylenediamine in tetrahydrofuran to give dianions. (43, 118)

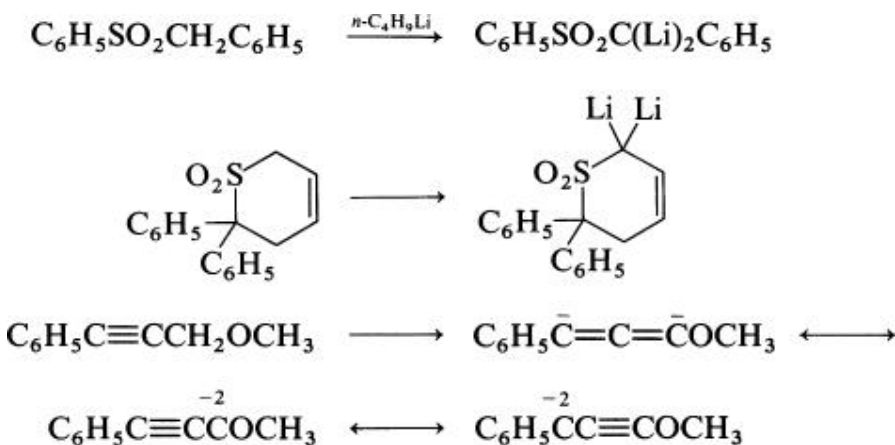


Dicarbaniions like **26** and **27** were prepared in a similar fashion. (119, 120)



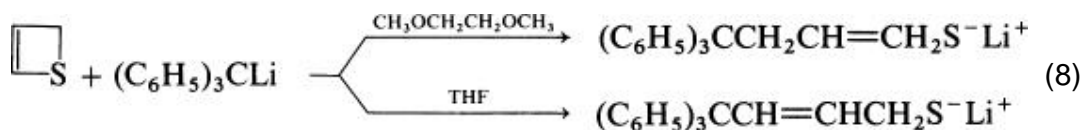
The latter, **27**, is stable only in the presence of lithium bromide.

The following *gem*-dicarbaniions were prepared from benzyl sulfones, (55, 121-123) allyl sulfones, (92) and propargyl ethers: (124, 125)



*sec*-Butyllithium (126) is more reactive and more sterically hindered than *n*-butyllithium. With alkyl allyl ethers *n*-butyllithium in tetrahydrofuran at  $-65^\circ$  does not react; by contrast *sec*-butyllithium produces the allylic carbanion. (127) However, *n*-butyllithium under the same condition reacts with phenyl allyl ethers. (32) The presence of a phenyl group seems to have a noticeable influence on the metalation rate. (32, 104) For triethylsilyl allyl ether, *sec*-butyllithium is a very efficient base. (32) With allyl thioether and derivatives *sec*-butyllithium was used. (45, 129-131)

Triphenylmethylithium attacks both the allylic carbon and the double bond of thiacyclobutene (Eq. 8). (132)



In N-methyl-1,4-dihydropyridine the vinylic proton at C-2 is removed by *n*-butyllithium and potassium *t*-butoxide, while the allylic proton at C-4 is removed by trimethylsilylmethyl potassium. (132a)

Lithium, sodium, and potassium amide in ammonia are efficient bases. (49, 133-135) More hindered amides like lithium diethylamide, diisopropylamide, isopropylcyclohexylamide, and 2,2,6,6-tetramethylpiperidide allow access to carbanions where other metalating agents give complex reaction mixtures. The amides are usually prepared *in situ* from amine and *n*-butyllithium, and the compound to be metalated is then added.

The reaction of organolithium (RLi) with boranes leads to a complex by addition of R<sup>-</sup> to the boron atom. However, with lithium 2,2,6,6-tetramethylpiperidide this addition can be avoided and the carbanion is formed in good yield. Lithium diisopropylamide and isopropylcyclohexylamide were inefficient in this reaction. (17)

Nitrosoamines give in excellent yield the corresponding anion with lithium diisopropylamide. With other reagents, the reaction is more complex. (23) The metalation rate of nitrosoamines by lithium diisopropylamide is greatly enhanced in the presence of potassium *t*-butoxide. (135a)

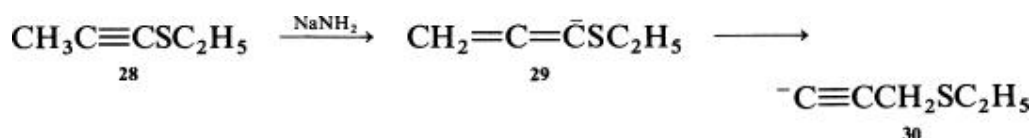
Allyl and benzyl benzamide can be converted to the dianion with lithium diisopropylamide. 135b,c



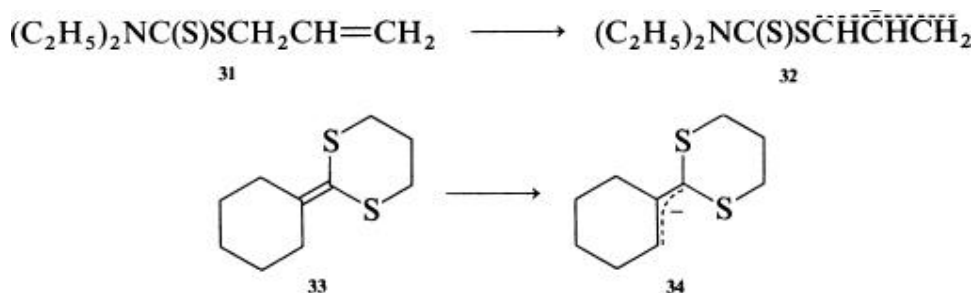
When the carbanion  $\text{CH}_2=\text{CH}\bar{\text{C}}\text{Cl}_2\text{Li}^+$  is prepared from 3,3-dichloropropene and lithium 2,2,6,6-tetramethylpiperidide, some brominated product is found in the reaction products. This results from the presence of lithium bromide in the methyllithium used to prepare the amide and from chloride–bromide exchange in the final product. The side product disappears after removal of lithium bromide by triglyme addition to the methyllithium solution. (135d)

The propargyl thioether  $\text{CH}_3\text{SC}\equiv\text{CCH}_2\text{OCH}_3$  and acetal  $\text{CH}_3\text{SC}\equiv$

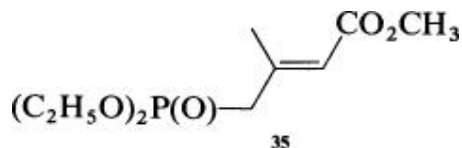
$\text{CCH}(\text{OC}_2\text{H}_5)_2$  are converted to carbanions by lithium diisopropylamide and diethylamide in tetrahydrofuran. (136, 137) With sodium amide in ammonia the allenic carbanion **29** produced from **28** is isomerized to **30**. (133)



Allyl N,N-diethyldithiocarbamate **31** and the ketene ketal **33** give the carbanions **32** and **34** with lithium diisopropylamide in tetrahydrofuran. (138, 139)



The preparation of carbanions from sulfoxides is improved by the use of a lithium dialkylamide. (140-142) In tetrahydrofuran–hexamethylphosphoramide, the phosphonate ester **35** can be converted to the anion by lithium isopropylamide. (143)



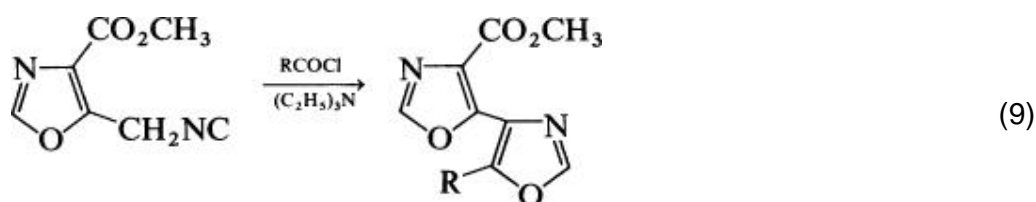
The attack of many reagents on selenoethers or selenoxides occurs at the selenium atom. However with lithium dialkylamide metalation occurs cleanly. (58, 59, 144)

Organomagnesium compounds have been seldom used as bases. For example, phenyl prenyl sulfone is reported to be metalated by ethylmagnesium

bromide. (145)

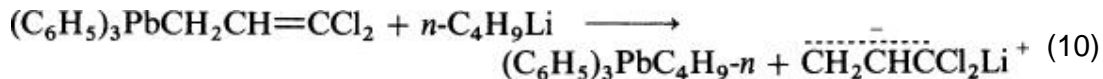
Potassium *t*-butoxide has occasionally been used as a base with isonitriles and sulfones. (146-148) Also, it was used as an additive to butyllithium as mentioned above.

Alkali hydrides usually react slowly. The higher temperature required for complete metalation may be harmful to the carbanion and lead to decomposition products. Allylic phosphonates can be metalated by sodium hydride in dimethoxyethane or in the presence of hexamethylphosphoramide. (149-151) Isonitriles and dithioacetals in dimethylformamide are transformed to the corresponding carbanions by the same reagent. (152, 153) Potassium hydride was used for the production of carbanions from allyl sulfoxides in tetrahydrofuran. (154) In the presence of a stabilizing substituent and a reactive reagent, triethylamine may be sufficient for some isonitriles (Eq. 9). (154a)



### 3.3. Transmetalation

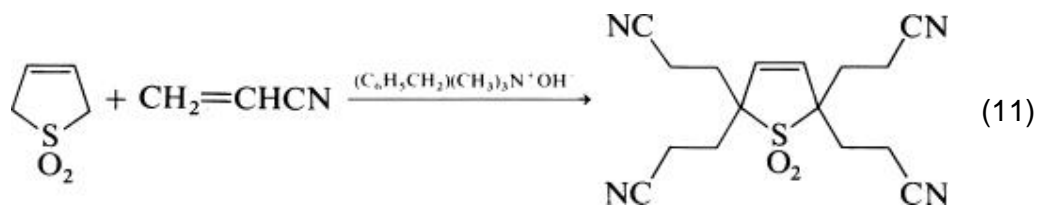
This method was used to prepare dichloroallyllithium from a plumbane by the action of *n*-butyllithium in tetrahydrofuran at  $-90^{\circ}$  (Eq. 10). (155)



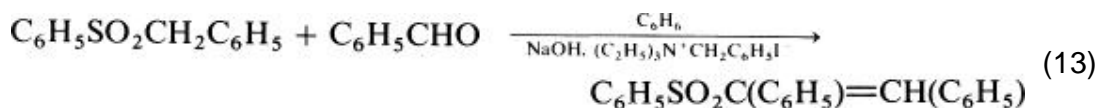
### 3.4. Phase Transfer

Probably because of the low acidity of most of the starting materials, phase transfer has seldom been used to generate carbanions. One early example of its use is the reaction 2,5-dihydrothiophene-1,1-dioxide with acrylonitrile in the presence of trimethylbenzylammonium hydroxide as a catalyst (Eq. 11). (156) All four hydrogen atoms react and no products from





ring opening of the intermediate carbanions are detected. Under the usual metalation procedure the carbanion undergoes a rapid electrocyclic ring opening. In phase transfer, where the carbanion is generated in the presence of the reactant, the lifetime of the intermediate carbanion may be short with respect to the half-life of rearrangement or elimination. The Horner reaction and the condensation of sulfones with aldehydes were performed in excellent yield by phase transfer (Eqs. 12 and 13). (157, 158)

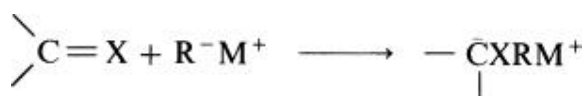


### 3.5. Halogen–Metal Interchange

This method has been used very little, probably because the starting materials are not readily available and the reaction of the generated carbanions with the starting material is difficult to control. The action of *n*-butyllithium on benzotrichloride and 1,1,1-trichloro-2-propene gives at  $-100$  to  $-105^\circ$  the lithium compounds  $\text{C}_6\text{H}_5\text{CCl}_2\text{Li}$  and  $\text{CCl}_2\text{CHCH}_2\text{Li}$ , the latter in a yield of ca. 50%. (159, 160)

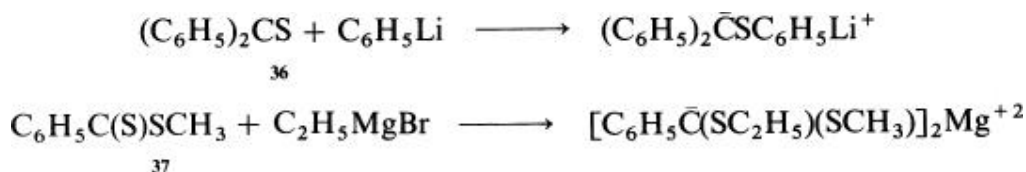
### 3.6. Addition

Carbanions can be generated by addition of a carbanion to  $\text{>C}=\text{X}$  double bonds:

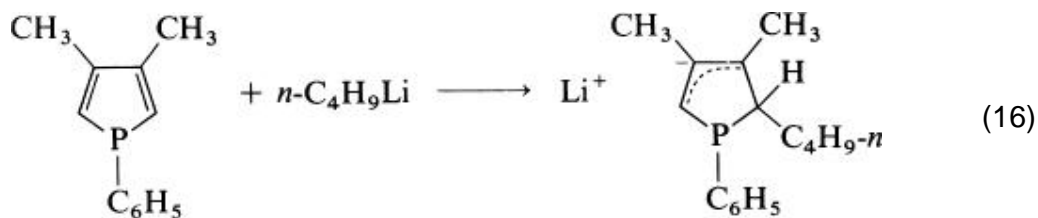
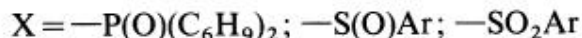
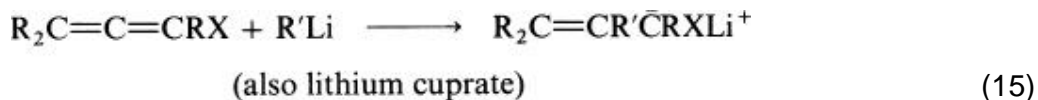
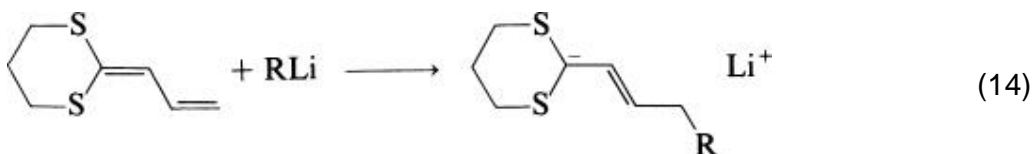


or by addition to activated double bonds.

Examples of the first mode are the reactions of organomagnesiums and lithiums with aromatic thioketones **36** and dithioesters **37**. (56, 161-163)

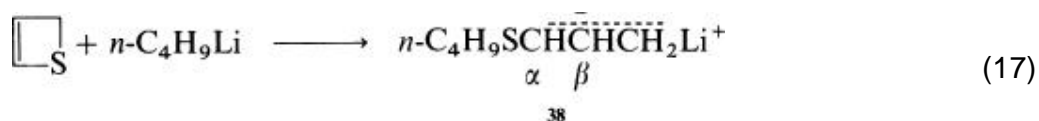


The second method is illustrated by the addition of lithium compounds to a ketenethioketal (**164**) (Eq. 14), to such heteroatom-substituted allenes as phosphine oxides, (**165-167**) sulfoxides, **166** and sulfones **166** (Eq. 15), and to phospholes (**167**) (Eq. 16).



### 3.7. Fragmentation

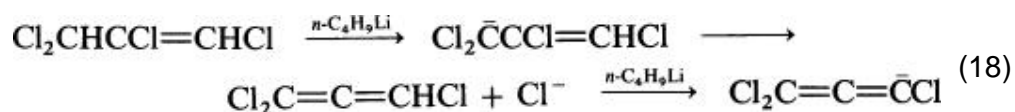
The reaction of *n*-butyllithium, as contrasted to the earlier discussion involving triphenylmethyl lithium, with thiacyclobutene takes a somewhat unusual course. Attack on the sulfur occurs and ring opening gives the allylic carbanion **38** (Eq. 17). (132)



This method of generation of the carbanion **38** may control its stereochemistry, while the alpha- beta bond should be *cis* if rotation around this bond is slow. This point awaits further investigation.

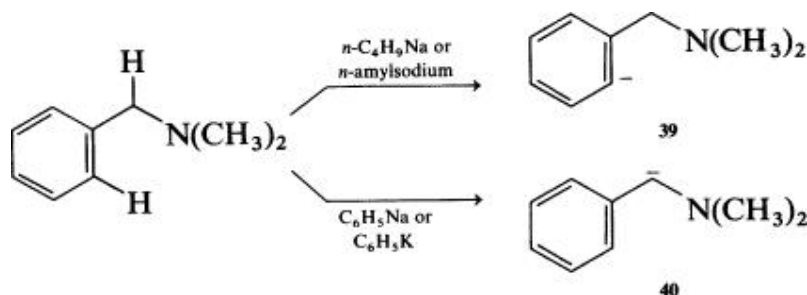
### 3.8. Comments

1. There are a few examples of carbanions not derived directly from starting material, since the initially formed carbanion may undergo an elimination to form a species that is subsequently metalated (Eq. 18). (168)



There are other such examples in the literature. (169, 170)

2. The addition to the basic medium of a solution containing the compound to be metalated and the electrophilic reagent has seldom been tried for obvious reasons. (38) However, the method might be useful for unstable carbanions. The carbanion formed from benzyl isothiocyanate is rapidly trapped by ketones. If a solution containing benzyl isothiocyanate and a ketone is added to potassium *t*-butoxide in tetrahydrofuran, then the addition compound is obtained. (22)
3. Isomerization of carbanions can be used in some cases. The action of *n*-butyl- or *n*-amylsodium on *N,N*-dimethylbenzylamine in hexane produces the *ortho*-metalated species **39**, which undergoes slow isomerization to the side chain anion **40**. The benzylic anion **40** is produced directly by phenylsodium or phenylpotassium. (18)



In conclusion, if one is faced with the problem of generating a carbanion for the first time from a species believed to be acidic, the following procedure is recommended. The commercially available and previously titrated *n*-butyllithium should first be tried. (95-98) One equivalent of base is added to a solution containing the product to be metalated in the presence of an amine, preferably redistilled N,N,N $\phi$ ,N $\phi$ -tetramethylethylenediamine in tetrahydrofuran. All operations must be performed under nitrogen or, better, argon, at  $-78^\circ$ . During the addition the solution is observed and color changes are noted. The appearance of a color that deepens as more *n*-butyllithium is added may indicate a stable carbanion (or a rapid decomposition of the carbanion to a colored species). A transient color during the addition could suggest the decomposition or a rapid rearrangement of the carbanion. In general the solution of carbanion described here is colored even if only faintly yellow although it is far from certain whether the color is attributable to the carbanion.

In trial experiments it is convenient to add (at  $-78^\circ$ ) deuterium oxide (diluted in tetrahydrofuran) to the reaction mixture 1 hour after addition of *n*-butyllithium. The deuterium content of the product is determined by spectroscopic examination. Three situations may be encountered:

1. The starting material is recovered with *no* deuterium incorporation. The metalation most likely did not proceed, so a more powerful base should be tried: *sec*- or *t*-butyllithium or a lithium dialkylamide or a combination like *n*-butyllithium–potassium *t*-butoxide.
2. The starting material has incorporated deuterium. The carbanion was obtained and is apparently stable under these conditions. Further exploration of the reaction conditions may improve yields.
3. No starting material is recovered. The *n*-butyllithium caused a reaction other than proton removal, carbanion decomposition or rearrangement. Further studies of the reaction product can give the answer. Lowering the temperature may slow down the decomposition or the rearrangement. A more specific base like a dialkylamide should be tried or the reactive group should be protected.

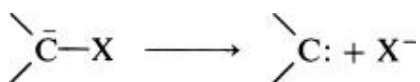
After it has been established that the carbanion is formed through its reaction with deuterium oxide, the next step is to study its reactivity with other reagents (see the section on reagents, p. 28). Usually reactions with halides, ketones, and epoxides proceed well. However, with these reagents it may be necessary to increase the reaction temperature or to add a more solvating solvent like hexamethylphosphoramide. The reaction time may vary from a few seconds to several hours. In many cases the discharge of the color or appearance of a precipitate may indicate a reaction.

## 4. Decomposition of Carbanions

Carbanions often undergo side reactions and disappear. Sometimes the products are not characterized and the literature may state that the carbanion decomposed. Yet, the decomposition reaction is clean and may be useful. Various side reactions are discussed in the following order: alpha, alpha'-beta, and other eliminations, cyclizations and ring openings, and migrations.

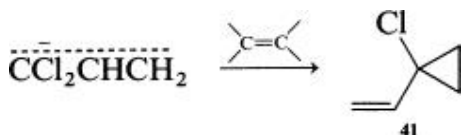
### 4.1. Eliminations

Alpha elimination gives rise to carbenes. This was observed with the



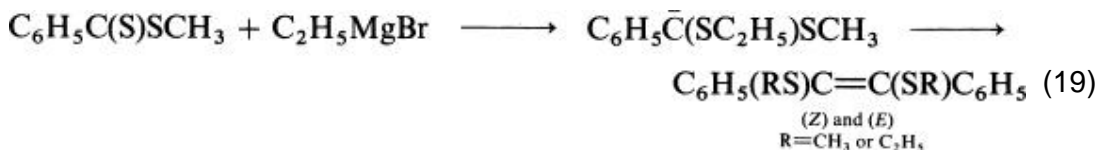
carbanion derived from benzylidene chloride, which at  $-65^{\circ}$  decomposed to phenyl chlorocarbene. The carbene was trapped by addition to

2,3-dimethyl-2-butene. (160) The carbanion  $\text{CCl}_2\text{CHCH}_2$  is also unstable at  $-65^{\circ}$  (159) and the decomposition of this intermediate in the presence of an olefin gives the vinylcyclopropane 41. (135a)

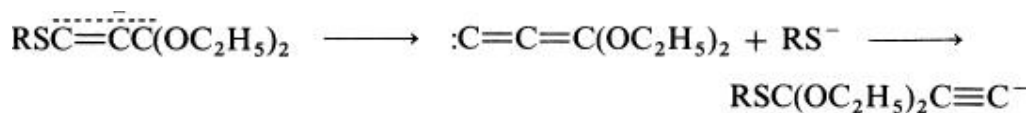


Alpha elimination was also noted with the carbanion  $\text{C}_6\text{H}_5\text{C}^{\ominus}\text{HOC}_6\text{H}_5$  and there was isolated the adduct derived from the addition of carbene to isobutylene. (171)

The carbanion formed on addition of ethylmagnesium bromide to a dithioate (Eq. 19) gives on standing a mixture of olefins that probably arises from alpha elimination and subsequent coupling. (163)



The following sequence was postulated for alpha elimination-addition to the carbene. (137)



The alpha $\phi$ -beta elimination of carbanions has received little consideration,



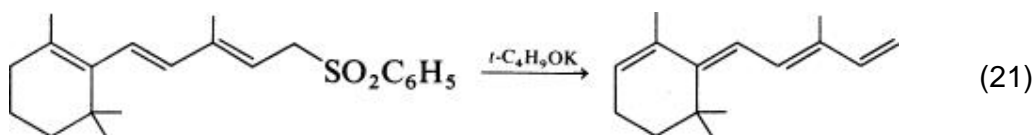
but its occurrence was observed accompanying the Wittig rearrangement of ethers. (172-177) The carbanion from benzyl cyclohexylmethyl ether gives methylenecyclohexane. (178)

Thioethers undergo alpha $\phi$ -beta elimination in high yield, (179, 180) probably because 1,2 rearrangement seldom occurs. The carbanion of benzyl *sec*-butyl thioether is stable at low temperature ( $-78^\circ$ ) but gives at  $25^\circ$  in 83% yield a 5:1 mixture of 1- and 2-butene. (179) The carbanion of benzyl *n*-octadecyl thioether undergoes alpha $\phi$ -beta elimination more slowly to give 1-octadecene in 92% yield by refluxing in tetrahydrofuran for 4-5 hours. (179)

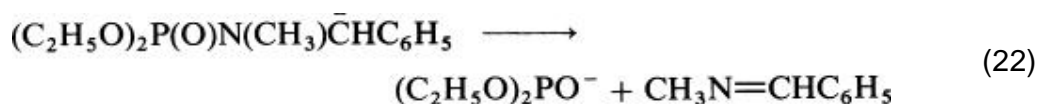
From the carbanions that can extrude an alkoxide group, the product is often metalated through subsequent reaction with base (Eq. 20). (181-183)



An elimination of a sulfone has been described (Eq. 21). (184)



The carbanion derived from bis(ethoxy)-*N*-benzyl-*N*-methylphosphoramidate and *n*-butyllithium undergoes elimination to produce imines that react further with *n*-butyllithium (Eq. 22). (27, 28)



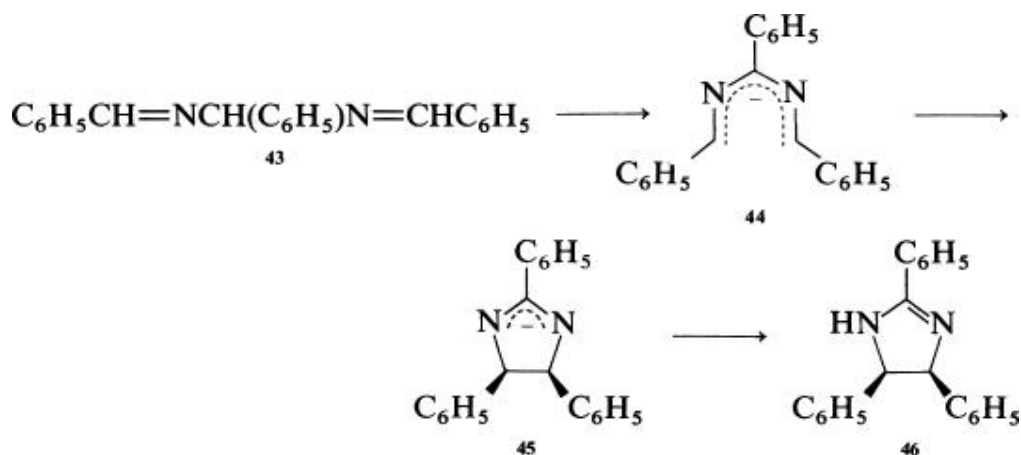
Bis(dialkylamino)-N-benzyl-N-methylphosphoramides give more stable carbanions. (185)

#### 4.2. Cyclizations and Ring Openings

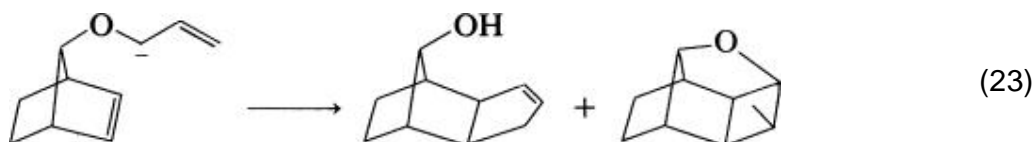
Several cyclizations have been described. The anion derived from a pyridyl isonitrile cyclizes to the anion **42**. (146)



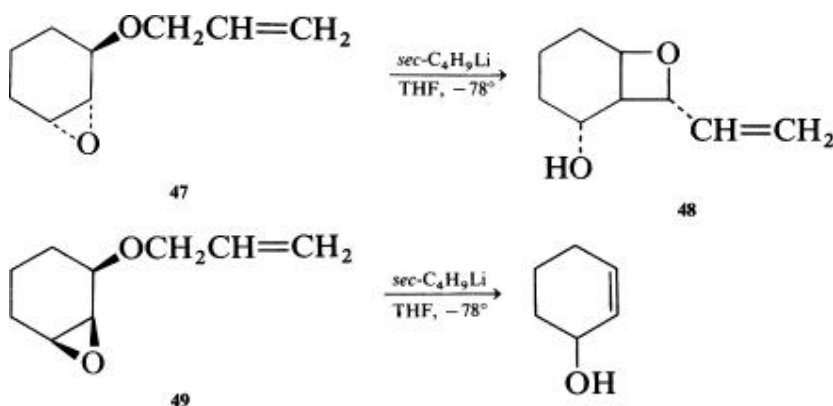
The base-catalyzed cyclization of hydrobenzamide **43** to amarine **46** occurs stereospecifically from the anion **44** prepared from hydrobenzamide in tetrahydrofuran and phenyllithium at  $-70^\circ$ . At this temperature the anion **44** has a half-life of 7 hours. Very likely a disrotatory  $6\pi$  electron cyclization of the U-shaped anion occurs so as to form the cyclized anion **45**. (186-188)



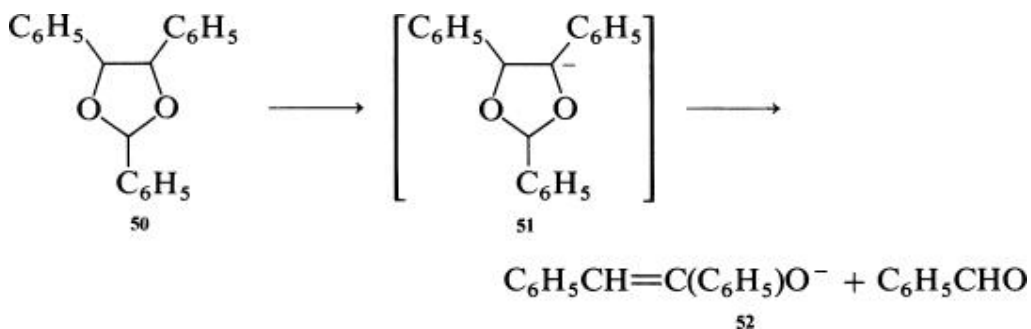
The intramolecular addition of carbanions derived from allylic and benzylic ethers to double bonds occurs in diethyl ether–tetrahydrofuran (Eq. 23). (189)



Intramolecular opening of the epoxide **47** forms the oxetane **48**, but the epimeric epoxide **49** fragments. (190)

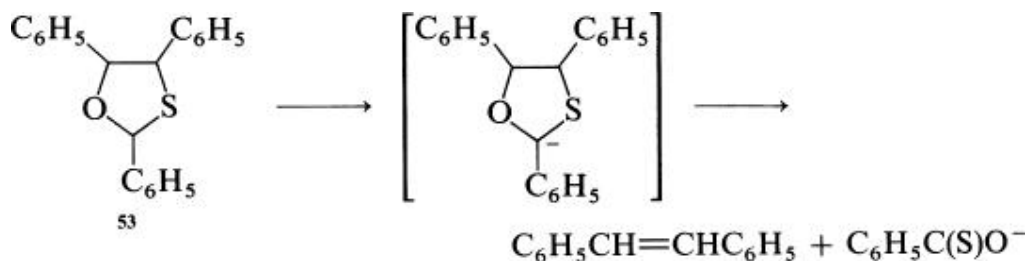


The cleavage of ethylene acetals to ethylene and a carboxylate under the action of a base is well documented. In substituted systems other cleavages may occur. For example, in the ketal **50** the proton abstracted is not that derived from the aldehyde, but from the glycol; the anion **51** cleaves to enolate **52** and benzaldehyde. (191, 192)

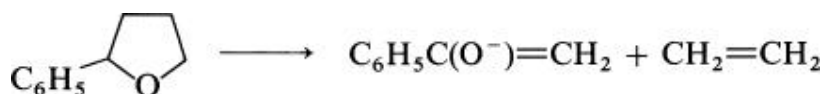




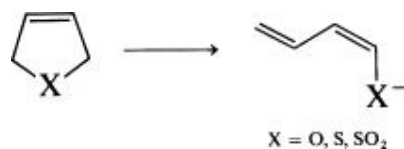
The monothioacetal **53** is metalated at the acetalic site and fragments to stilbene and thiocarboxylate. (35)



The analogous cleavage of 2-phenyltetrahydrofuran to tetrahydrofuran is described. (176)



Ring opening of the anions derived from 2,5-dihydrofuran, 2,5-dihydrothiophene and its 1,1-dioxide, and 2,3-dihydrooxepin is quite rapid at  $-60^\circ$ . (193) This reaction corresponds to the reversal of cyclization of hydrobenzamide to amarine discussed above.



### 4.3. Migrations

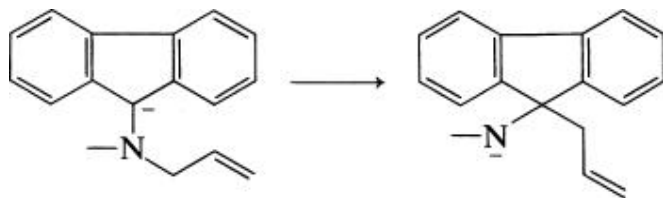
A number of migrations are observed in which the group on the heteroatom migrates to the carbanion part. These migrations, often occurring in high yield, may have preparative value. Migrations may sometimes be avoided by changes in the nature of the group on the heteroatom (often not of much importance because this group will be removed later) or by changes in reaction conditions such as temperature, solvent, or counterion.

In contrast to the extensive studies of migration in ylides derived from quaternary ammonium salts, migrations in carbanions derived from nitrogen

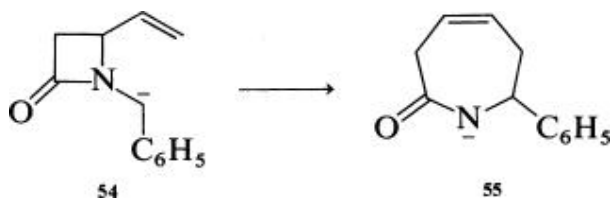
have been little explored. In analogy to the Wittig migration, the carbanion of N,N-diphenylbenzylamine slowly (72 hours) undergoes at 25° a 1,2 migration. (194)



Sigmatropic shifts have been described (195) and used for ring enlargement of

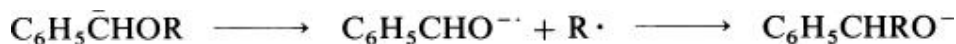


$\beta$ -lactams. The  $\beta$ -lactam is metalated to the carbanion **54** at  $-78^\circ$  with



lithium diisopropylamide in tetrahydrofuran, and it is likely that this carbanion undergoes a rapid concerted [2,3]sigmatropic shift to amide anion **55**. With steric hindrance and aromatic groups, products arising from nonconcerted migration may appear. (196)

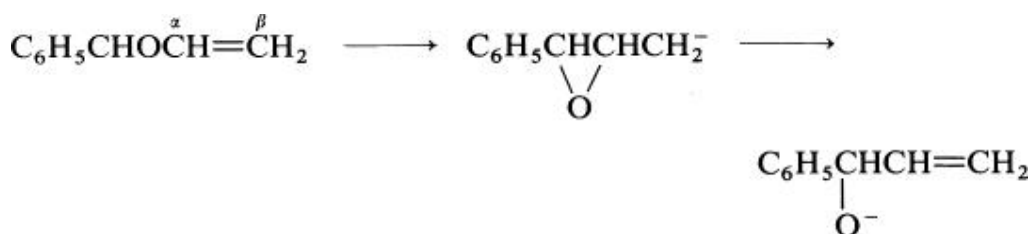
Migrations in carbanions derived from ethers were extensively studied, but here we report only the essential points. Many different alkyl and aryl groups are known to undergo 1,2 migration in the Wittig rearrangement. The migration rate depends on the nature of the cation. (94, 197) This migration has been shown to be largely but not completely intramolecular, (198) occurring with partial racemization. (199, 200) The rate of migration is related to the dissociation energy of the hydrocarbon corresponding to the migrating radical. (174) These facts suggest that the Wittig rearrangement is a free-radical process, the carbanion dissociating to a radical-anion and a radical that recombine essentially in the solvent cage to give an alkoxide. (177)



For migration of a phenyl group the formation of benzyne as an intermediate was excluded. (201) The migration of a vinyl group has been observed without isomerization of the double bond. (202)

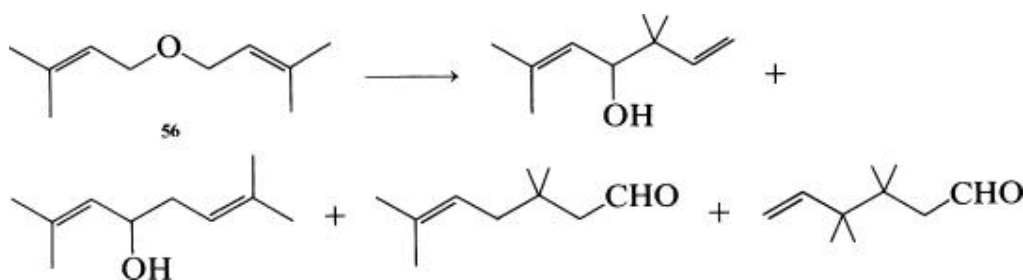


This result may be explained by fragmentation to aldehyde and vinyl lithium. An alternative explanation involves an intramolecular addition of the carbanion to the double bond followed by opening of the epoxide. Ring opening is more rapid than rotation around the alpha - beta bond. (202)



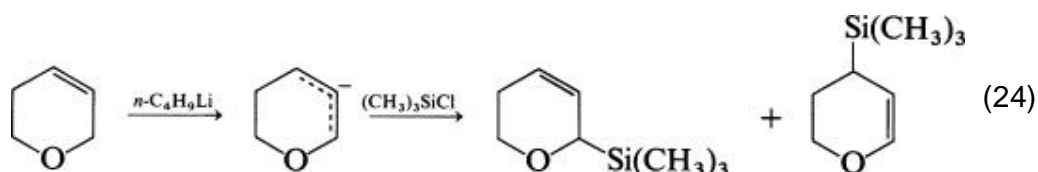
Both 1,4 and 1,2 shifts of carbanions prepared from allyl ethers were simultaneously observed. (203) They occur with 30% racemization for the carbanion of allyl  $\alpha$ -phenylethyl ether. (204) A nmr study of this type of rearrangement showed that the rearranged products are not polarized. However, a short relaxation time may be the reason for the lack of observable polarization in the product of the Wittig rearrangements. Thus a free-radical path is not excluded. (205) Migrations of silyl and of phosphorus groups from oxygen or from sulfur to the anionic carbon have been described. (31, 36, 47, 50, 206, 207)

Carbanions derived from diallyl (56) and allyl benzyl ethers undergo

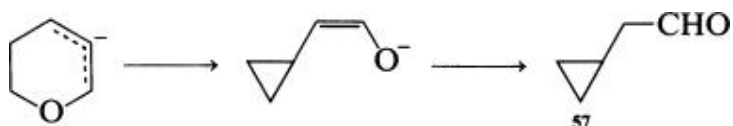


rapid rearrangements, among which [2,3]sigmatropic shifts may be concerted. (208-213) A cyclopropane group can replace the double bond. (214) The [2,3]-sigmatropic shifts occur suprafacially for both fragments. (211)

Dihydropyran gives with *n*-butyllithium a carbanion that reacts with trimethylsilyl chloride to yield two products (Eq. 24). 215



At higher temperature a [1,4]sigmatropic shift occurs to form the cyclopropylaldehyde **57**. A concerted mechanism is proposed for this rearrangement. 215



Carbanions derived from diallyl thioethers and derivatives undergo [2,3]sigmatropic migrations even at  $-78^\circ$  that are faster than the metalation. (180, 216)

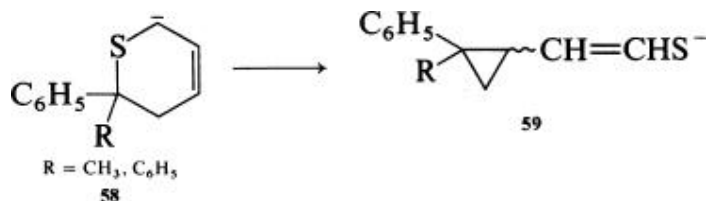


However, under isomerization conditions (sodium ethoxide–ethanol) vinylic thioethers are produced beside the rearranged products. (217) The benzyl and allyl-*N,N*-dimethyldithiocarbamates with *n*-butyllithium give carbanions that are stable at  $-78^\circ$  in tetrahydrofuran, but in the presence of hexamethylphosphoramide they undergo a 1,2 shift. (218)

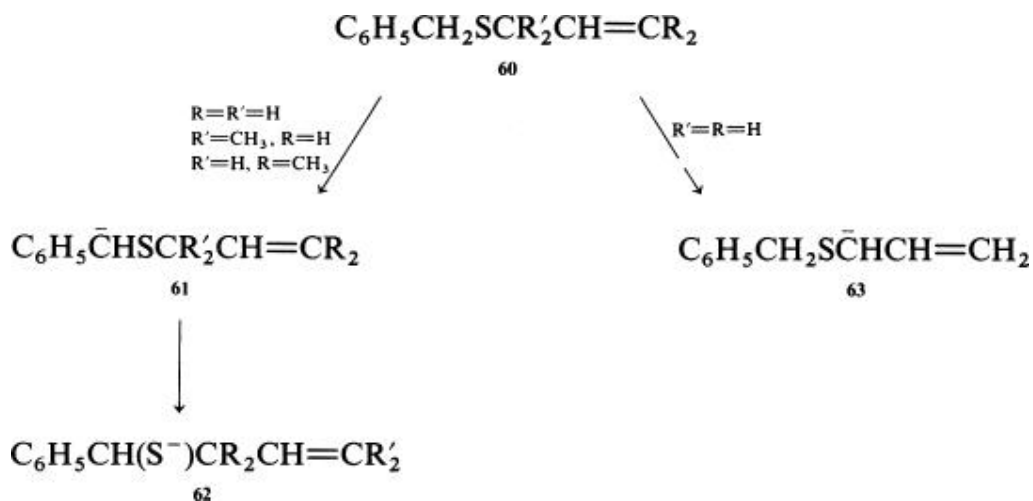


The carbanions **58** from 4-thiacyclohexene (with a phenyl substituent next to the sulfur) are stable at  $-78^\circ$ . The carbanion **58** undergoes rearrangement to a

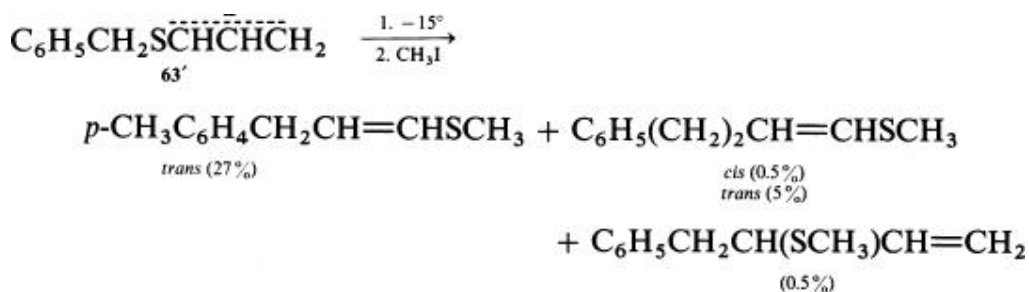
vinylcyclopropyl compound **59** at higher temperature in a proposed stepwise mechanism. (219, 220)



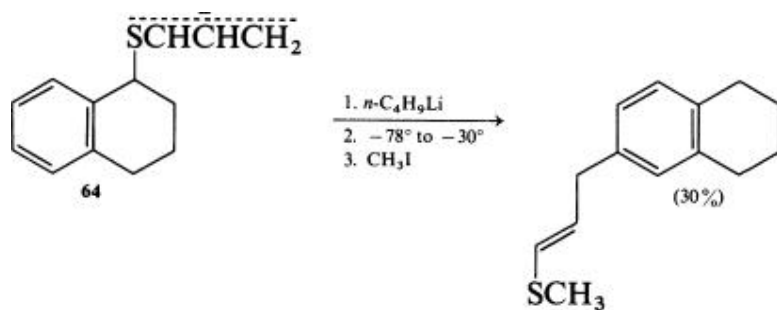
The allyl benzyl thioether **60** can give, depending on the substituent on the allyl radical, two different carbanions: the benzylic **61** that rearranges rapidly to thiolate **62**, and the allylic carbanion **63** that is stable at  $-78^\circ$ . (180, 216, 221)



At higher temperature the allylic carbanion **63**, redrawn as **63'**, undergoes various rearrangements. (216, 219)



The intriguing migration into the *para* position is also observed in a tetralin system **64**. (221)



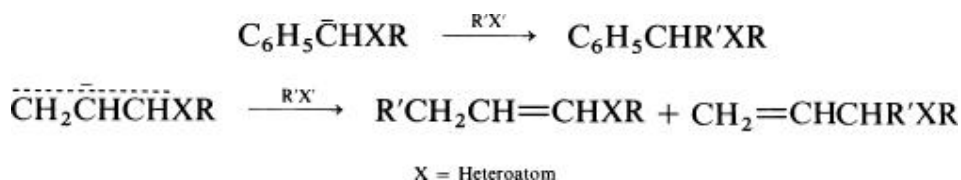
Dibenzyl thioether gives at  $-78^\circ$  a stable carbanion that rearranges at higher temperature essentially by two pathways: a [2,3]sigmatropic shift, analogous to the Sommelet rearrangement, and a [1,2]shift, similar to the Wittig rearrangement. The competition between both rearrangements depends on the temperature and the solvation of the cation. Higher temperatures favor the [1,2]shift and a solvating medium permits a [2,3]sigmatropic shift. (222, 223)

Decompositions and rearrangements can be controlled during metalation by variation in reaction conditions. Such variations include a more selective base, such as a lithium dialkylamide instead of *n*-butyllithium, a lower temperature, another solvent, or a different substituent at the heteroatom. On the other hand some of these reactions occur in high yield, while the yield of others can be improved by use of proper conditions. Their preparative value is still to be exploited.

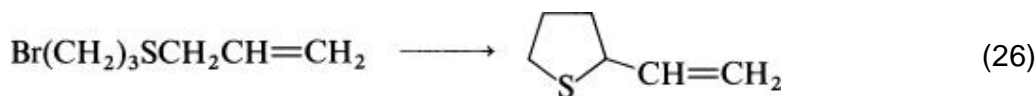
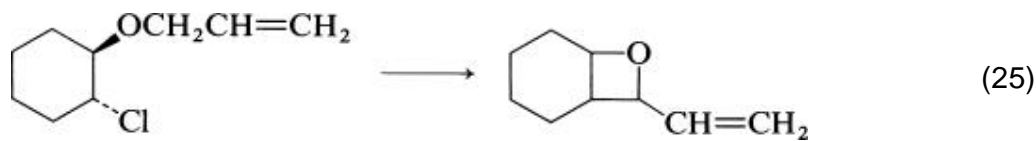
## 5. Reactions with Electrophiles

A large variety of reagents have been used, but this is certainly a field where developments are to be expected; with new reagents new systems may be prepared. In this chapter we mention the common reagents only briefly and place more emphasis on the more exotic reagents.

Alkyl iodides, bromides, and chlorides are often used. Iodides and bromides are preferred because the chlorides are less reactive. Sometimes elimination



instead of alkylation of the carbanion is the main reaction. (224) The rate of alkylation with a halide seems to vary from very fast, often described as instantaneous, to slow, with carbanions from allyl phenyl sulfoxides. (225) The rate may be increased by addition of hexamethylphosphoramide to the tetrahydrofuran solution. (226) Several intramolecular cyclizations of carbanions bearing a halogen have been observed and are illustrated by Eqs. 25-27. (190, 227, 228)

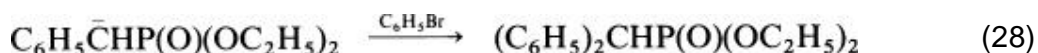


Tertiary halides have seldom been used, probably because of the prejudice

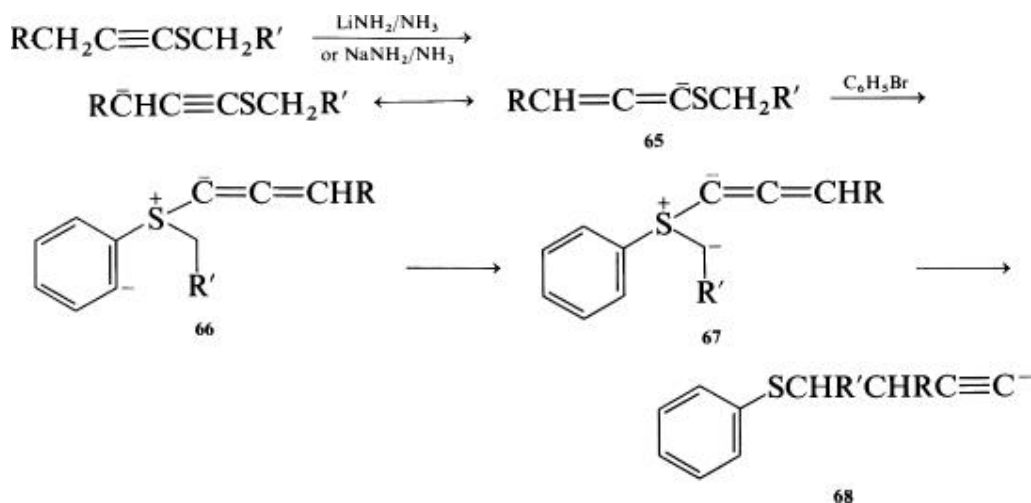
that elimination would be the main reaction. But in several instances the reaction with a *t*-butyl halide proceeds with good yield. [228a,b](#) An electrophilic catalysis by the lithium cation has been proposed on the basis that after addition of 12-crown-4 the reaction is very slow. ([228a](#)) In one case neopentyl iodide and tosylate did not react. ([228a](#))

Sulfonate esters are claimed to be inefficient in most cases. Toluenesulfonates and methanesulfonates are acidic, and proton transfer may proceed faster than alkylation. Benzenesulfonates could be more useful. ([229](#)) However, reaction at a sulfur atom may occur, as has been found with some carbanions. ([230](#)) Other sulfonate esters such as trifluoromethanesulfonates or fluorosulfonates are scarcely mentioned in the literature. Sulfonate esters have recently been used as electrophiles with stabilized carbanions. [231a,b](#)

Aromatic halides are expected to be of little use, yet some reactions with bromobenzene are described in the literature. Most likely benzyne is produced by reaction of the carbanion with bromobenzene and adds to the excess carbanion (Eq. [28](#)). ([232](#), [233](#))

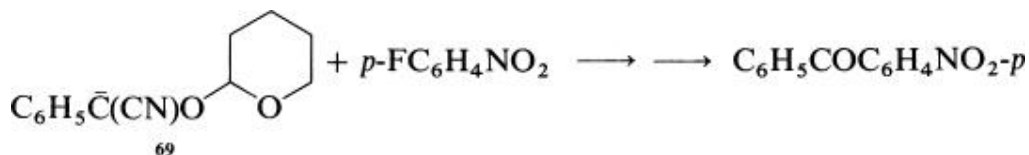


A rearrangement is described that may result from a sigmatropic shift of an ylid carbanion. ([234](#)) Benzyne is postulated to react with the carbanion [65](#) to produce the ylid carbanion [66](#), which undergoes a proton shift to another ylid carbanion [67](#). Finally a sigmatropic shift of this latter ylid carbanion gives the anion [68](#).





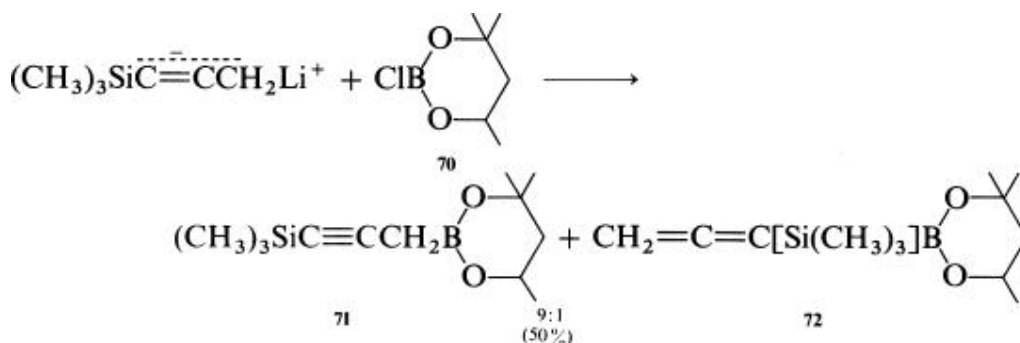
With carbanion **69** reaction with activated *p*-nitro- and 2,4-dinitrofluorobenzene occurs. (235)



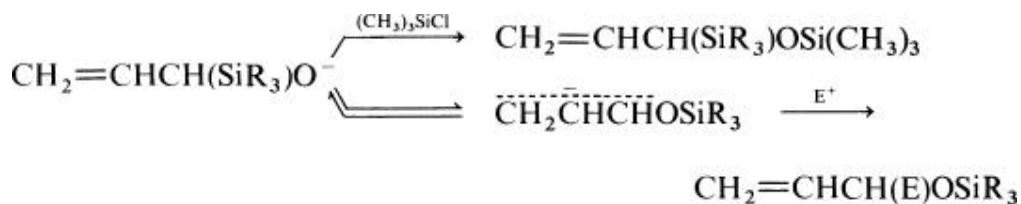
Polychlorinated hydrocarbons, e.g., carbon tetrachloride and tetrachloroethylene, react with carbanions to form chlorides. (236, 237) The reaction of methylene chloride may be of some interest for the synthesis of the substituted [1.1.0]bicyclobutane system (Eq. 29). (238)



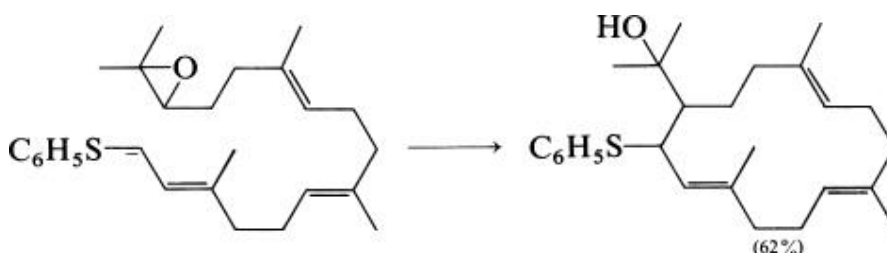
Condensation of a halogenoboronate **70** with a carbanion gives access to alkyl boronate esters **71** and **72**. (239)



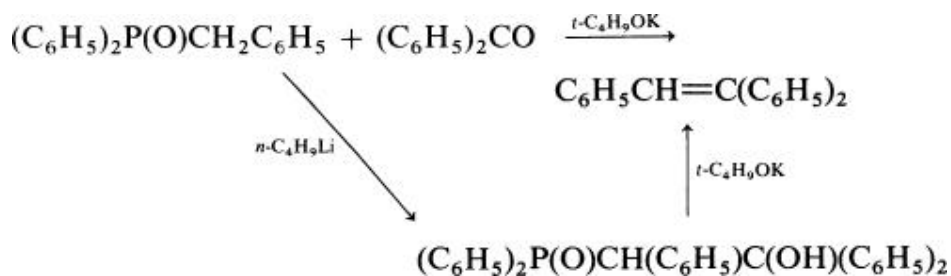
Trimethylsilyl chloride is commonly used to study carbanions. More complex chlorosilanes, as well as triethylbromogermane and triphenylchlorostannane, react with the carbanion derived from phenyldithiane. (240) These reagents open the area of diheterosubstituted systems. In addition, trimethylsilyl chloride reacts with alcoholates, and the resulting silyl ether anion can add electrophiles at the carbon atom. 240a,b



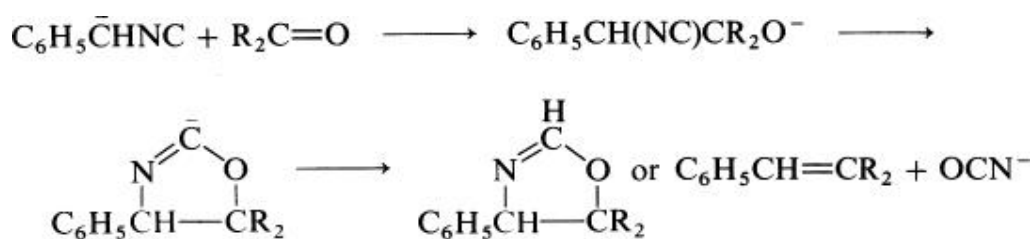
Epoxides react with carbanions in the expected way. (142, 228, 241)  
 Intramolecular cyclizations at the epoxide proceed in good yield, (190, 242)  
 including the synthesis of a 14-membered ring system. (237)



The reaction of heterosubstituted carbanions with aldehydes and ketones is trivial except for several instances where other reactions follow, e.g., carbanions alpha to phosphonate, phosphine oxide, or isonitrile groups. In the case of phosphonates and phosphine oxides, the alkoxide product of the first reaction undergoes a further reaction leading to an olefin with a simultaneous elimination of the phosphonate or phosphine oxide group and the alkoxide. (38, 243, 244) The intermediate can sometimes be isolated. (38)

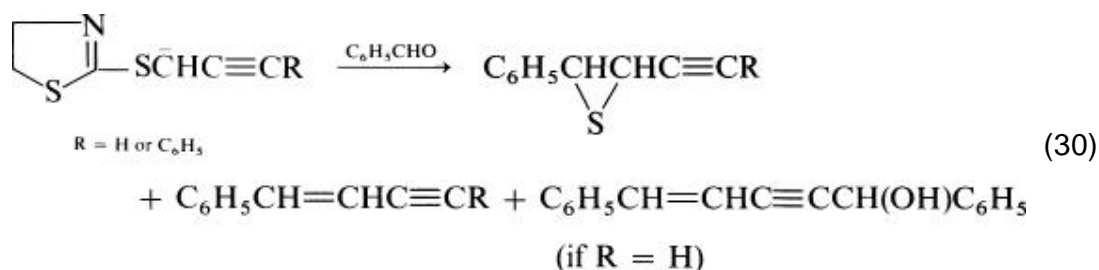


Carbanions alpha to an isonitrile react with carbonyl compounds, yielding cyclic systems that may undergo cycloelimination to an olefin and isocyanate anion on heating. (21, 146, 245, 246)



A similar cyclization was described for the reaction of a carbanion alpha to a thioisonitrile. (22)

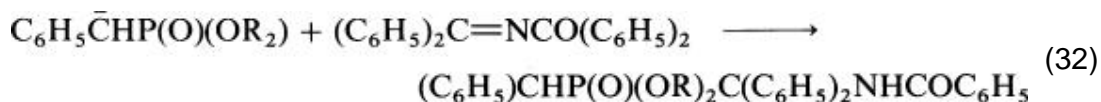
Another example of an elimination leading to an episulfide and an olefin is the reaction of the carbanion derived from a propargylic thiothiazoline with benzaldehyde. (247) The intermediate alkoxide attacks the thiazoline ring, and this results in a migration of the ring followed by intramolecular displacement (Eq. 30).



A dianion next to a sulfone reacts with aldehydes and ketones to give vinylic sulfones (Eq. 31). (122, 123)

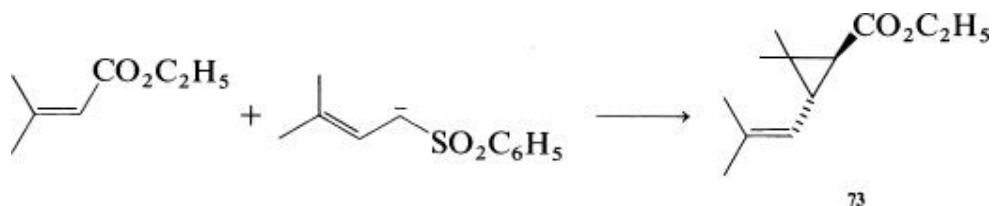


N-Benzoylketimines react with carbanions alpha to a phosphonate (Eq. 32). (135)

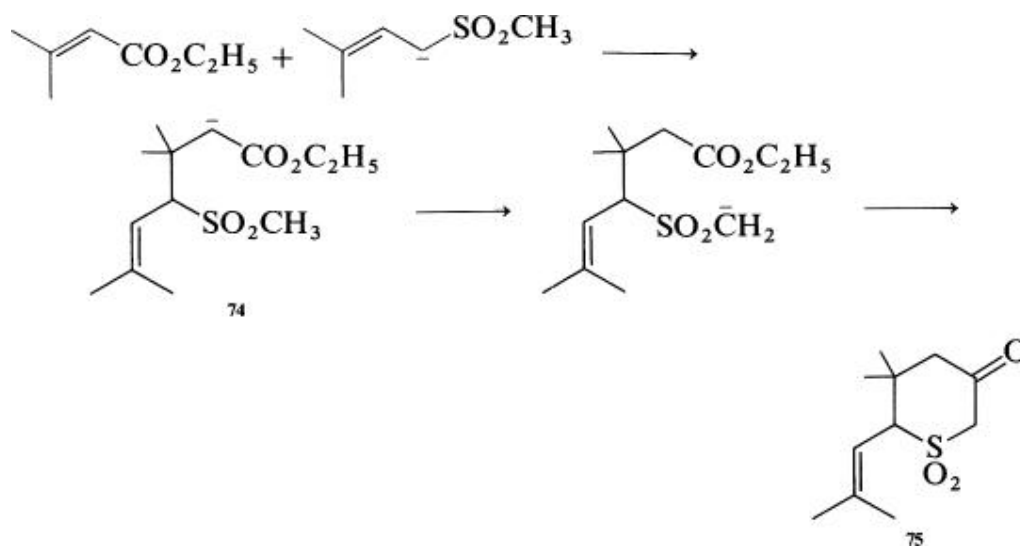


Conjugate addition of heterosubstituted carbanions to  $\alpha$ ,  $\beta$ -unsaturated electrophiles (ketones, esters, lactones, and nitro compounds) sometimes

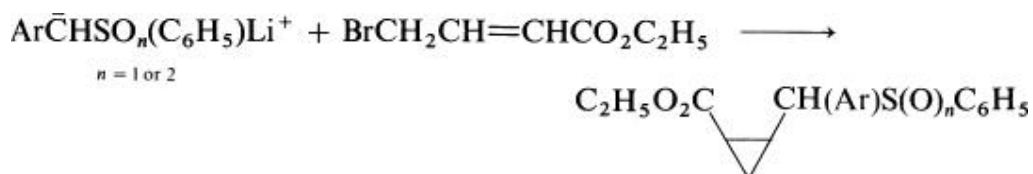
occurs. (248-250) This addition is favored by the transformation to lithium cuprates. (251) The carbanions derived from allylic sulfones add to  $\alpha$ ,  $\beta$ -unsaturated esters in a 1,4 addition, which in turn is followed by a displacement of the sulfone by the carbanion next to the ester to yield a cyclopropane **73**. (252)



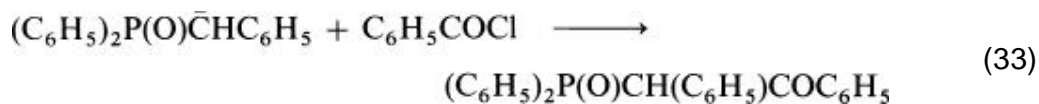
Phenyl sulfones give better yields of cyclopropanes than do methyl sulfones. In the latter proton transfer in the addition compound is possible, leading to a different cyclization, **74** & **75**. (253)



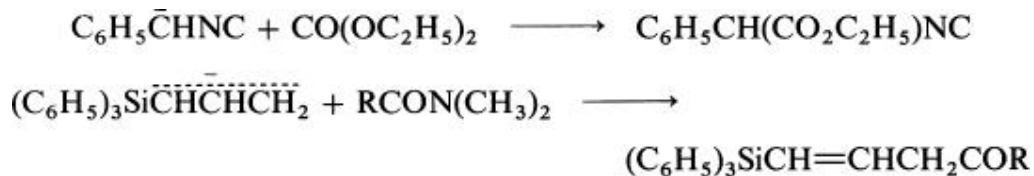
Conjugate addition of a carbanion alpha to a sulfoxide or a sulfone to ethyl 4-bromo-2-butenoate leads to a cyclopropane. (253a)



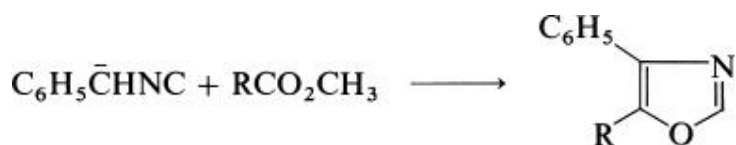
Acid chlorides have been scarcely used; however, on reaction with carbanions alpha to a phosphine oxide, ketones are produced in good yield (Eq. 33). (254)



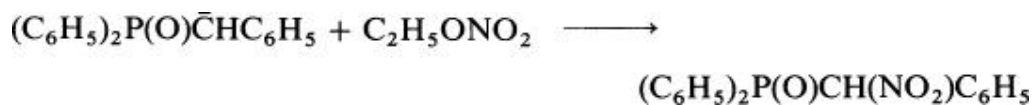
Amides and diethyl carbonate are convenient reagents in several cases: (152, 255, 256)



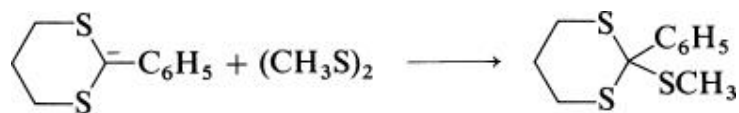
Reaction of esters with carbanions alpha to an isonitrile yields oxazoles. (256)



Nitro compounds can be prepared by reaction of nitrates with carbanions derived from phosphine oxides. (257)



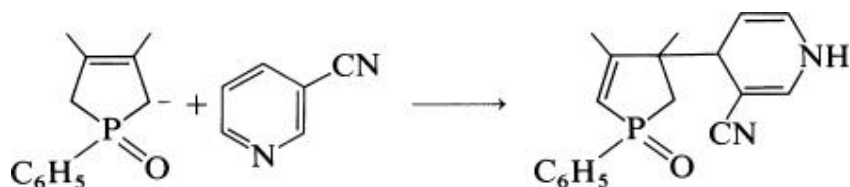
The reaction of disulfides with carbanions gives thioethers. (139, 258, 258b)



Sulfur has been used to produce a thiol in good yield. (258c)



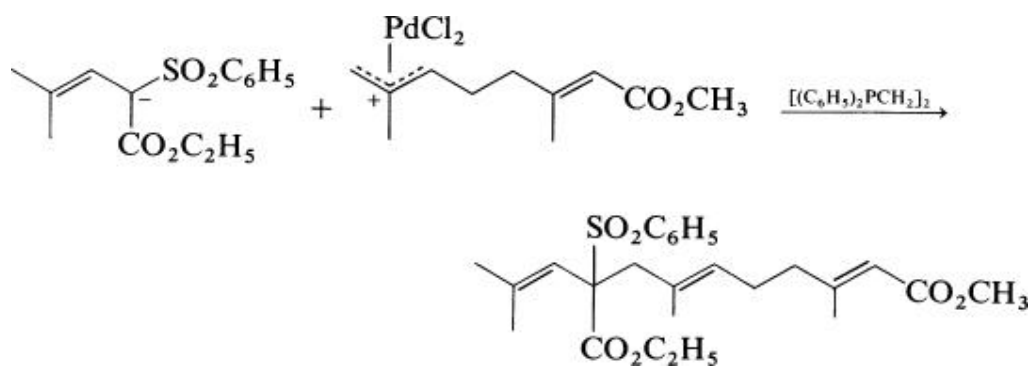
The addition of heterocyclic systems has been little explored: it is known, however that the anion from phosphol-3-ene oxide adds to the ring of nicotino- and isonicotinitrile. (259)



Reaction of iron pentacarbonyl with the carbanion derived from benzaldehyde ethylene dithioacetal, followed by methyl iodide, gives 1-phenylpropane-1,2-dione (Eq. 34). (260)

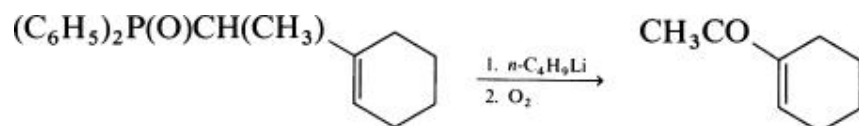


$\pi$ -Allyl palladium derivatives activated by a phosphine can act as electrophiles. (261)



Oxygen, which often gives complex reaction mixtures, seems to be efficient in the reaction with the carbanion derived from a substituted phosphine oxide.

(262)



There appear to be no examples of the use of a heterosubstituted carbanion to synthesize organometallic derivatives.

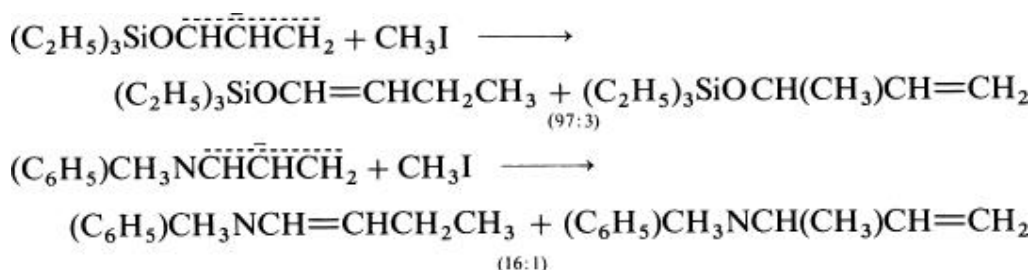
## 6. Regioselectivity

Allylic ambident carbanions contain two centers, alpha and gamma, where reaction can occur:



The regioselectivity depends on a number of factors. An attempt has been made to correlate regioselectivity and electron distribution. (263) It is certainly unwise to draw conclusions about the location of the cation from the regioselectivity. In some cases the possibility of equilibration, leading to thermodynamic control of the reaction course, is excluded. Nevertheless it is necessary to point out here the factors that have an influence on the regioselectivity, without speculating on the structure of the carbanion. With a knowledge of these factors one may be able to direct the reaction to the desired position and this is clearly of preparative value. Among the known factors are the nature of the heteroatom, the substituent on the heteroatom, the substituent on the allylic system, the nature of the conjugated system, the electrophile, the counterion, and the solvation. The effect of temperature has been little explored, essentially because the temperature range is limited by the stability of the carbanion and by the solvent system.

In general, carbanions derived from allylic ethers and allylic amines have a strong tendency to react with alkyl halides at the gamma position. (19, 26, 32, 101-103, 113, 127, 264, 265)

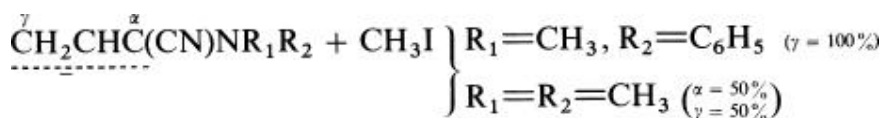


The reason for the regioselectivity may well be the location of the cation at the gamma position, where it may be stabilized by chelation with the heteroatom. (90, 266) This agrees with the *cis* stereochemistry of the vinylic double bonds in the reaction products. A similar argument could explain the regioselectivity of the reaction from the dianion of allyl thiol. (43, 221, 267) The carbanions from allylic thioethers, sulfoxides, sulfones, and selenides tend to react with

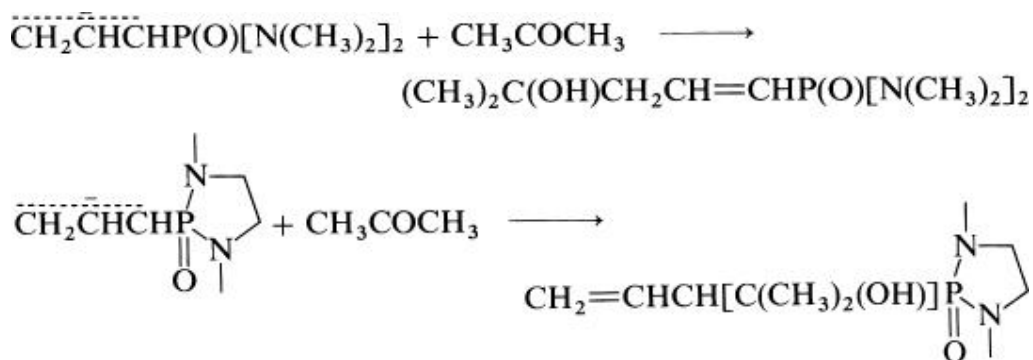


alkyl halides at the alpha position. Those derived from boranes and silanes have not been explored sufficiently to conclude whether the regioselectivity is caused by the nature of the heteroatom or by other factors.

The nature of the substituent on the heteroatom may be of great influence; the different behavior of allylic thioethers and allylic thiols has already been mentioned. The influence of the substituent is not easy to understand. Certainly steric factors have some importance but do not explain all the observed facts. Also intramolecular solvation of the cation by the substituent may play a role. An increase in the size of the substituent, as expected, increases the proportion of alkylation at the gamma position. (20, 32, 42, 268)



The effect of the substituent on the heteroatom has been studied mostly with carbanions derived from allylic thioethers. The high reactivity at the alpha center of carbanions derived from allylic thioethers containing substituents that are able to chelate the lithium : 2-pyridyl, (269) imidazolyl, (46, 270) and dimethyl dithiocarbamate, (48) is still of questionable origin. A 4-pyridyl substituent yields a similar product ratio and intramolecular chelation is not possible. (8) The carbanion derived from allyl phenyl thioether gives at  $-78^\circ$  an alpha : gamma ratio of 75:25 with methyl iodide whereas that derived from allyl benzyl thioether gives a ratio of 98:2. (8, 82, 221) A change in the amine group in allyl phosphonodiamides gives almost complete control over regioselectivity. The reaction with acetone changes from gamma to alpha when the substituent is changed from bisdimethylamino to dimethylethylenediamino. (42)



The introduction of an alkyl substituent at the alpha or gamma position decreases the reactivity of this center toward alkyl halides. For example, in allyl phenyl thioether the alpha:gamma ratio is 3:1, whereas in  $\gamma$ ,  $\gamma$

-dimethylallyl phenyl thioether and in 3-but-1-enyl phenyl thioether the alpha:gamma ratios are 98:2 and 70:30, respectively. (44, 144, 225, 271)

When the double bond is replaced by a triple or an allenic bond, the reaction tends to take place only at one center. Anions derived from propargylic ethers or from allenic ethers react at the gamma position with alkyl halides. (272-275)  
With the anion of propargylic thioketal,



the reaction occurs at the alpha position. With the carbanion

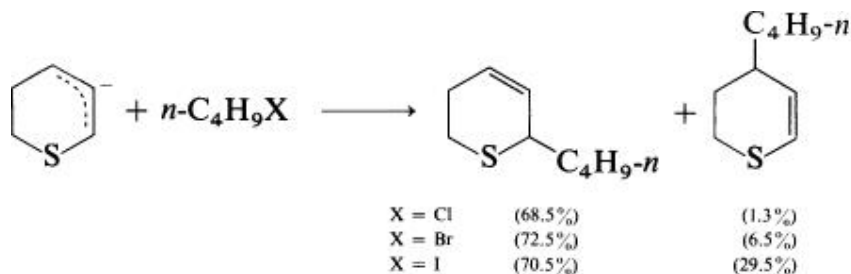


X = Heteroatom

prepared from acetylenic compounds  $\text{R}_2\text{CHC}\equiv\text{CX}$  or from allenic compounds  $\text{R}_2\text{C}=\text{C}=\text{CHX}$ , the reaction occurs almost exclusively at the alpha center, and the nature of the reagent has no influence. (273, 275-277)  
However, for the carbanion derived from ynamines  $\text{CH}_3\text{C}\equiv\text{CNR}_2$  the alpha center is favored with small substituents at nitrogen and the gamma center with more hindered ones. (20)

The variation of regioselectivity can reflect not only the ambident nature of the carbanion, but also different mechanisms. The reaction may occur by an  $\text{SE}_2$  mechanism through transfer of one electron followed by radical coupling or by cyclic addition, as may be the case for carbonyl compounds. Halides and ketones often exhibit opposite regioselectivity. (113, 264) The oxygenated

carbanion  $\text{RO}\overset{\ominus}{\text{C}}\text{HCH}_2$  reacts with the alkyl halides at the gamma center and with cyclohexanone at both alpha and gamma, the ratio depending on the nature of the group R on the oxygen. (127) Regioselectivity was most extensively studied in thioethers. With alkyl halides there are several examples where the alpha:gamma ratio (greater than 1) depends to some extent on the nature of the halogen and on the nature of R. (82, 130, 219, 278, 279)



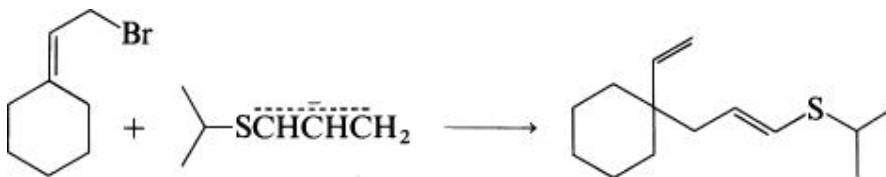
The reaction of ketones with these carbanions occurs essentially at the gamma position. (130, 278, 279)

The reaction with epoxides seems to occur at the same center as with halides for the allylic carbanion with nitrogen or sulfur, but some yields are low. (103, 278)

The alpha:gamma reactivity of the carbanions derived from allylic sulfoxides also depends on the nature of the halogen. (225, 271, 280) The regioselectivity of reactions of the dichloroallyl carbanion  $\overset{\cdot\cdot}{\text{C}}\text{Cl}_2\overset{\cdot\cdot}{\text{C}}\text{H}\overset{\cdot\cdot}{\text{C}}\text{H}_2$  was explained by the hard and soft acid-base concept: namely, soft acids such as acetone and cyclohexanone react at the soft center alpha and hard acids like hexafluoroacetone and benzophenone at the hard center gamma. (155, 159)

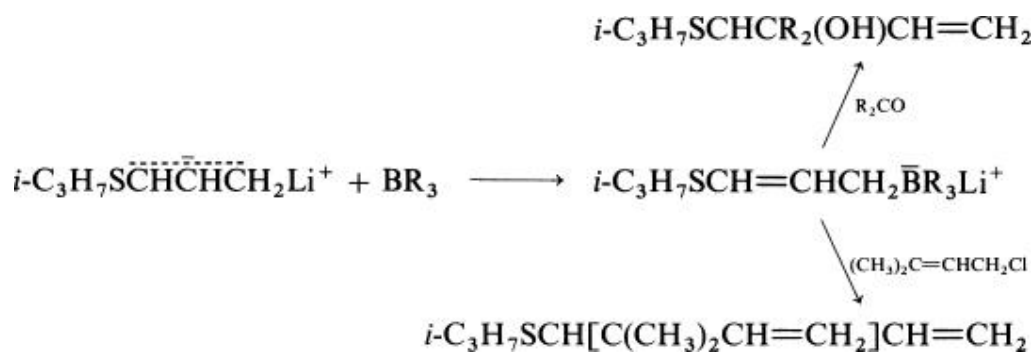
Leaving group dependence has been found for both silyl ether and dithiane-derived carbanions. The reagent with a soft leaving group reacts mainly at the gamma position for the silyl ether carbanion and at the alpha position for the dithiane carbanion. For reagents with a hard leaving group the alpha position is seen with the ether, while the gamma center is preferred for the dithiane. 231a,231b

The nature of the counterion may play an important role in the regioselectivity of the reactions. For the carbanion from allyltriphenylsilane the reactivity of the alpha center is enhanced with the magnesium derivative compared to the lithium salt of the carbanion. (108, 255, 281) Very often the addition of some salts to the carbanion solution is sufficient to change the regioselectivity. The reaction of the carbanions from methyl allyl ether or from phenyl  $\alpha$ -methylallyl thioether with carbonyl compounds occurs mostly in the alpha position after addition of zinc chloride, whereas in the lithium derivative the alpha and gamma carbons have similar reactivity. (30, 42, 127, 219, 281a, 281b) The addition of cuprous salts to the lithium salt of isopropylallyl thioether anion changes completely the regioselectivity of the reaction with allyl halides. In the following example reaction occurs at the gamma position of both reactants. (282, 283)



The regioselectivity depends on the nature of the ion pair present. This was shown for the anion derived from phenyl  $\gamma, \gamma$ -dimethylallyl sulfide, where the reaction with acetone occurs essentially at the  $\gamma$  center in tetrahydrofuran. However, after addition of cryptand[2.2.2], which leads at least to dissociated ion pairs, the reaction occurs only at the alpha center. (279)

Through a reaction with boranes the regioselectivity may be essentially reversed. For the lithium carbanion derived from allyl isopropyl thioether the addition of borane leads to an "ate" complex. Reaction with carbonyls then occurs mainly in the alpha position but without the borane there is some preference for the gamma position. (284a) Reaction with  $\gamma, \gamma$ -dimethylallyl chloride and bromide occurs at the alpha center with inversion of an allyl unit. (284b)



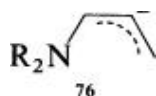
The nature of the final product in some cases may not reflect the real alpha–gamma regiospecificity. For instance, the reaction of the reagent derived from allyl phosphonate with ketones seems to occur only at the alpha center because only the alpha product can lead to phosphate elimination and double bond formation. The gamma product cannot give this elimination reaction but may be converted to the alpha product by a dissociation–addition process. (151)

By suitable choice of medium, reactant, and structure of the anion and the cation, the regioselectivity may be partially controlled.

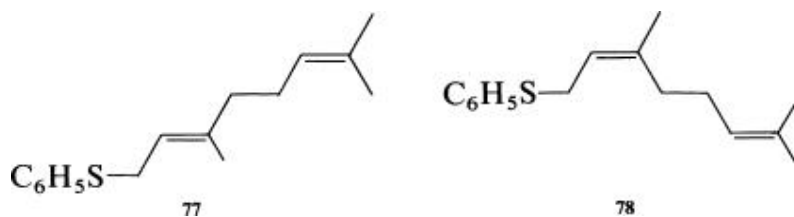
## 7. Stereochemistry

Little attention has been paid to the stereochemistry of the reactions of these carbanions.

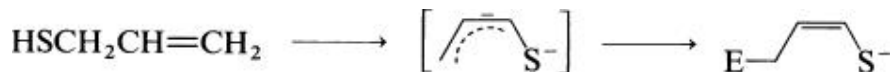
The stereochemistry of the double bond in the final product of the reaction of an allylic carbanion with an electrophile may reflect either the absence of isomerization at the carbanion stage or isomerization to a single isomer. The carbanion **76** exists to a great extent if not exclusively in the (*Z*) configuration and gives by reaction at the gamma center essentially the (*Z*) enamine. (90, 102, 103, 264, 265, 284)



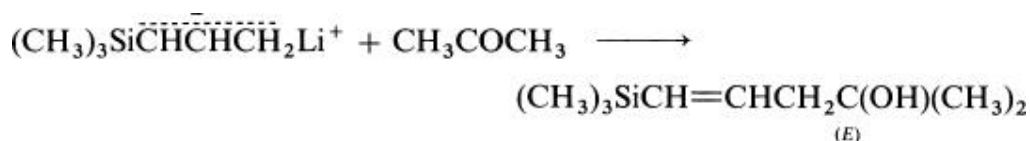
The carbanions derived from the two allylic thioethers **77** and **78** do not interconvert at  $-78^\circ$ . (87)



The dianion derived from allyl mercaptan is in the (*Z*) configuration and by reaction with electrophiles gives mainly the (*Z*) vinylic thioether (**43**) along with a small percentage of the (*E*) isomer. (221)

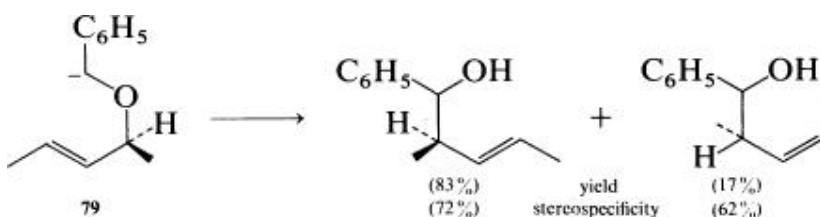


The silyl carbanion may exist essentially with (*E*) stereochemistry, as inferred from the stereochemistry of the reaction product with acetone. (284c)

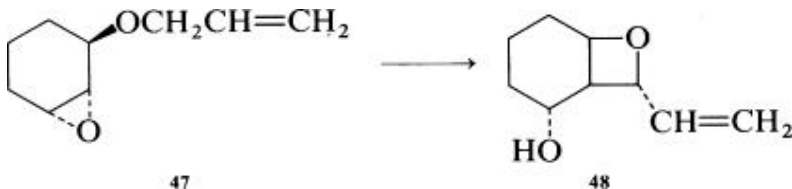


The 1,2 migration occurring in carbanions derived from benzylic ethers proceeds to a large extent with retention of configuration of the migrating group. (200)

The carbanion resulting from the metalation of (S)(+)-benzyl- $\alpha$ -D-oxytrimethylsilane undergoes a rapid intramolecular rearrangement to the oxyanion of (S)(-)- $\alpha$ -hydroxy- $\alpha$ -trimethylsilyl- $\alpha$ -D-toluene. Thus the rearrangement occurs stereospecifically with 99% inversion at the benzyl carbon. (285) A disrotatory cyclization of hydrobenzamide to amarine was previously discussed (p. 22). The transfer of stereochemistry of one center to another in a [1,4]sigmatropic shift is described for the carbanion 79. (211)

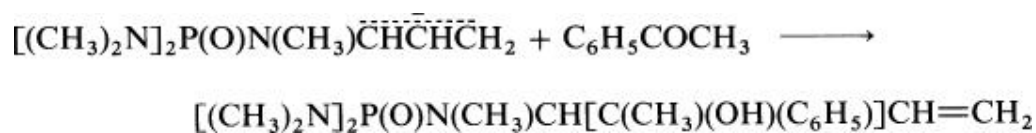


Intramolecular reactions may have a very strong preference for one isomer. The cyclization of the carbanion derived from the allyl ether epoxide 47 to the alcohol 48 occurs not only with inversion as expected at the oxirane center, but also with strong induction at the carbanionic center as expected from steric hindrance. (190)

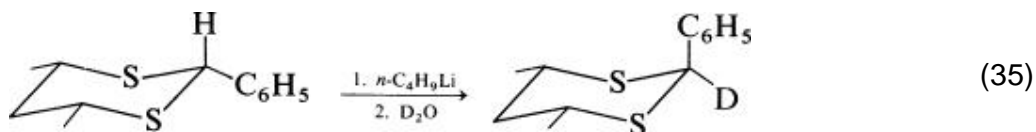


When two asymmetric centers are generated during a reaction, the ratio of diastereoisomers may differ from unity. An example is the reaction of acetophenone with the carbanion derived from

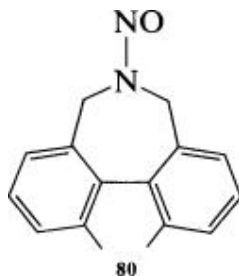
allylpentamethylphosphoramidate, where the ratio varies from 20 to 0.5 depending on the addition of lithium bromide and the solvent. (286)



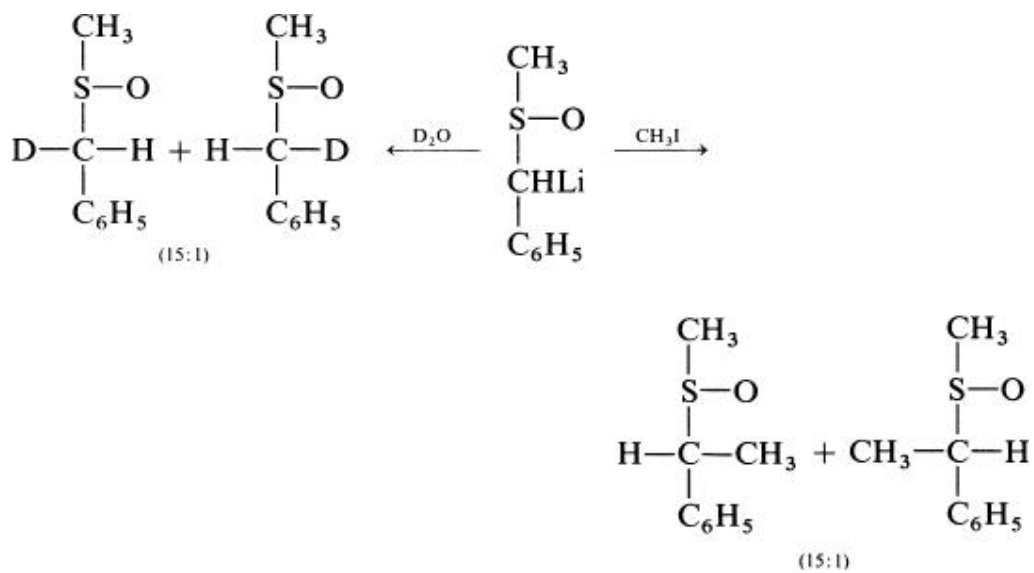
The preference for equatorial attack on conformationally rigid carbanions derived from a 1,3-cyclodithiane is assumed to be caused by a strong preference for the carbanion to be equatorial, (80) presumably because of stereoelectronic factors (Eq. 35). (78)



The asymmetry of the biphenyl system induces stereoselectivity in the reaction of carbanions derived from the N-nitrosoamine 80. (25)



The most-studied examples of asymmetric reactions are those given by carbanions alpha to sulfoxides. Even in open-chain systems 1,2 induction is high. (51, 91, 92, 287-292) This was initially attributed to stereoselective factors,



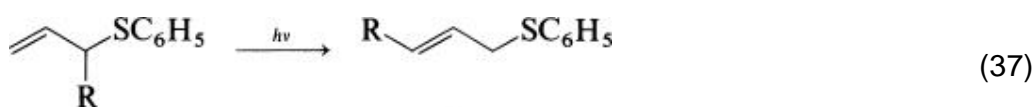
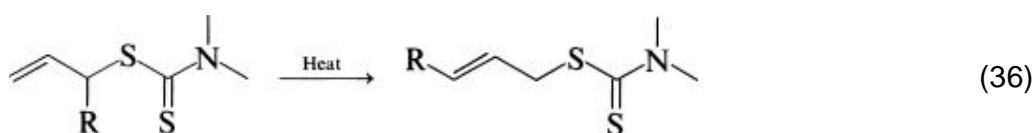
but clearly other factors such as internal solvation of the cation are also important. (91, 293) The racemization of the allylic sulfoxide limits this 1, 2 induction.



## 8. Transformations

The carbanions reviewed here are of great utility, since after reaction with electrophiles the products can often be easily transformed into other compounds, the heteroatom playing the role of a potential functional group. We consider here the migration of the activating functions, reductive removal, transformations into various other functions, and, finally, some ring-opening and ring-closure reactions.

The migration of a group in an allylic system makes possible the successive activation of two carbon atoms. Migration can be achieved by thermal rearrangement in the allyl dithiocarbamate (Eq. 36) (48) and by photochemical isomerization with the allylic phenyl thioether (Eq. 37). (294)



The heteroatom very likely increases the regioselectivity compared to that of the allylic anion, and in most cases this group will be removed later. The nitrogen-activating groups nitroso and isonitrile are transformed, respectively, to secondary or primary amines by acid treatment. (23, 152)



The elimination of the heteroatom often occurs by lithium—amine reduction using ammonia—ethylamine as demonstrated for some benzylamines (101) and for allylic phenyl thioethers. (87, 138, 242, 295-297)

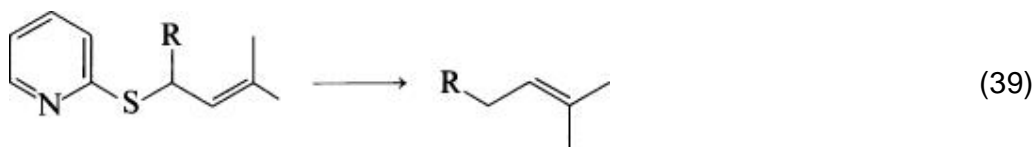
Raney nickel, which usually gives a complex reaction mixture with thioethers,

can be used for the reductive removal of the N-dimethyldithiocarbamate group. (298) Nickel boride seems to be useful for the removal of the phenyl thioether group. (298a)

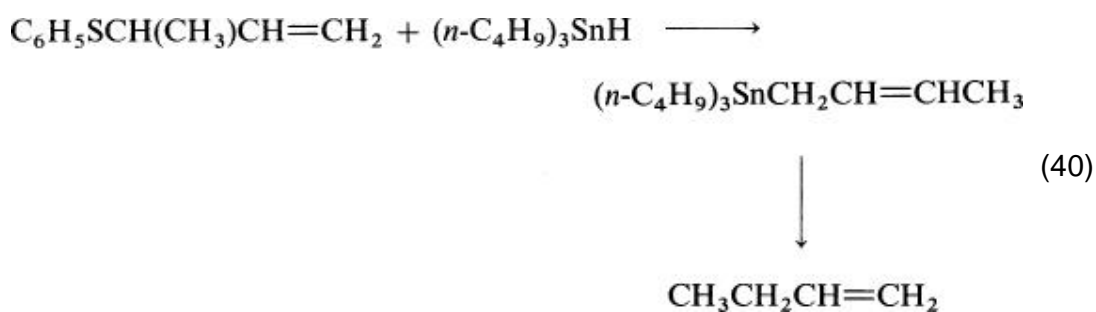
Lithium aluminum hydride removes the phosphonate group, apparently without migration of the double bond (Eq. 38). (299)



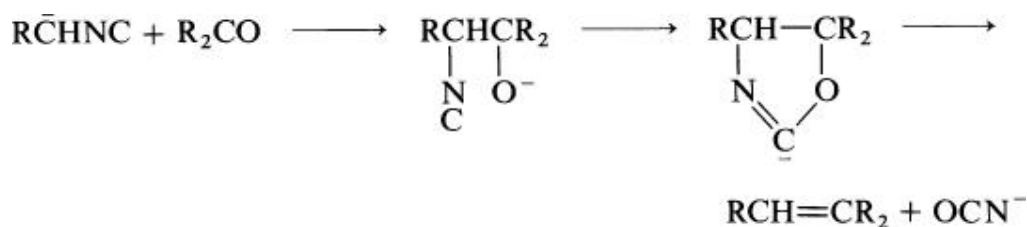
Addition of cupric salts to lithium aluminum hydride is necessary to promote the removal of the  $\alpha$ -thiopyridyl group, again without a double bond shift (Eq. 39). (269, 300)



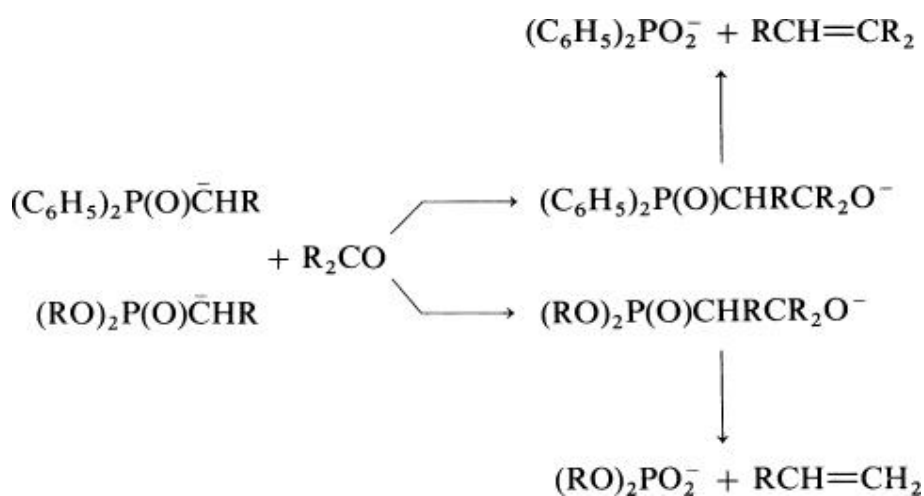
The displacement of an allylic or propargyl thioether or sulfone by tributyltin hydride occurs photochemically or by free-radical initiation in good yield. The acidic removal of the stannyl group leads to the olefin (Eq. 40). (300a, 300b)



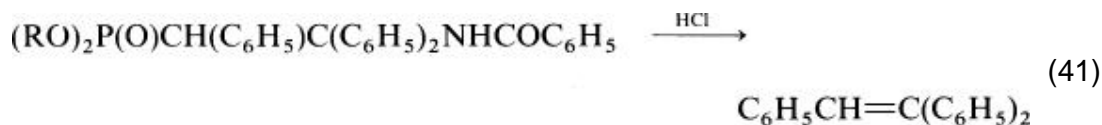
The elimination of the heteroatom to give an olefin is a very useful reaction. The reaction product from the carbanion of an isonitrile and a carbonyl compound may undergo cyclization and then eliminate isocyanate to produce an olefin. (21, 146, 245, 246)



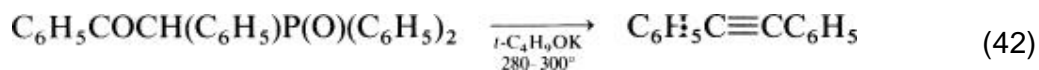
The final reaction product of carbanions from phosphine oxides or phosphonates with carbonyls is an olefin. (42, 262, 301-303)



With lithium as cation the hydroxy phosphine oxide can be isolated and converted to the olefin when treated with potassium *t*-butoxide. (38, 304) If imines instead of carbonyl compounds are used, the same reaction path occurs but under acid catalysis (Eq. 41). (135)



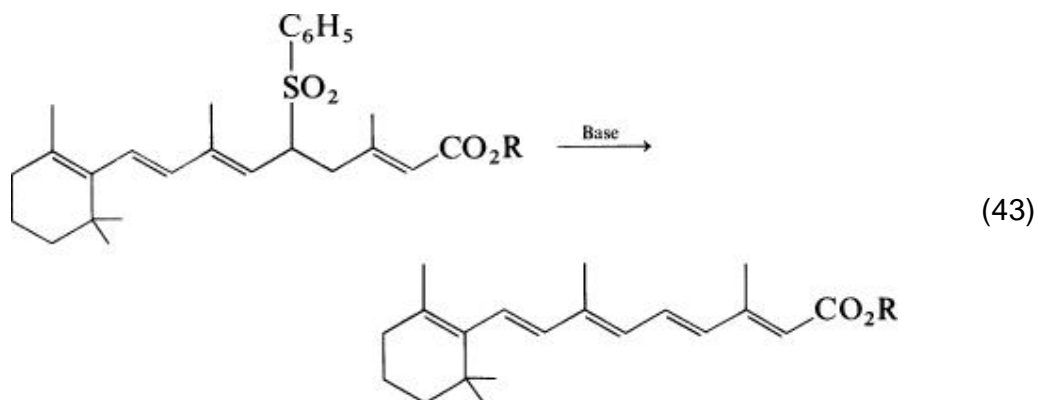
Under more vigorous conditions acetylenic compounds can be obtained from phosphine oxides (Eq. 42). (254)



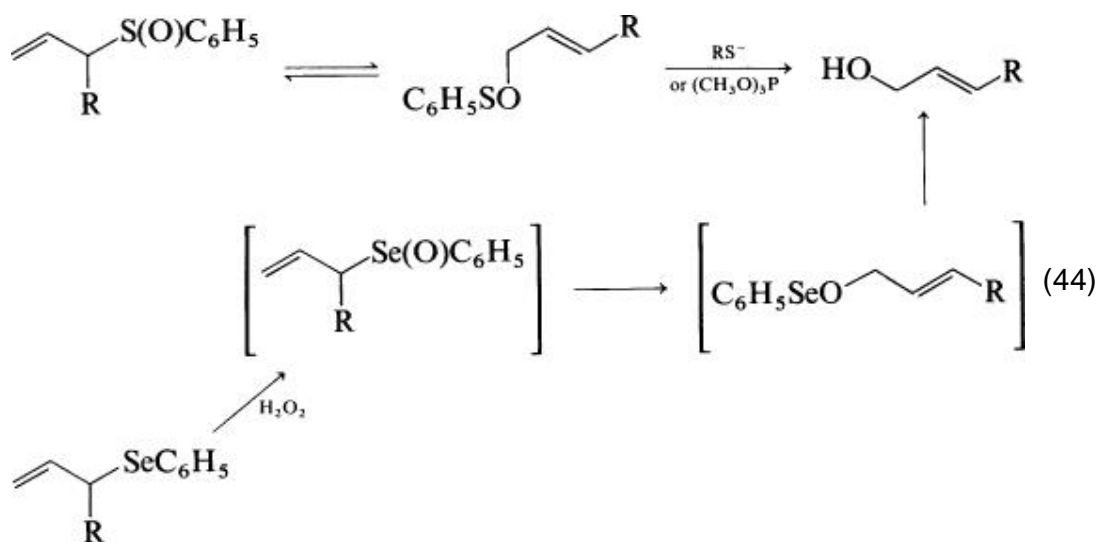
The thermal elimination of sulfenic acid from sulfoxides easily leads to olefins. The regioselectivity is influenced by substitution at the carbon atom from which

hydrogen is being eliminated. (141) A similar reaction is described for selenoxides prepared *in situ* from selenides. (58, 59)

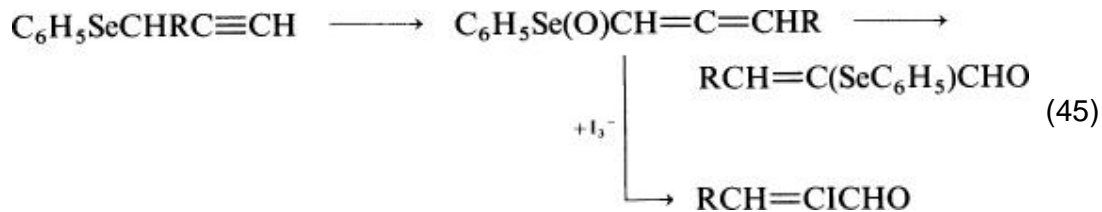
The elimination of sulfones takes place in the presence of base. (134) The reaction occurs easily if an activating group such as an ester is present, as illustrated in the synthesis of vitamin A (Eq. 43). (184, 305, 306)



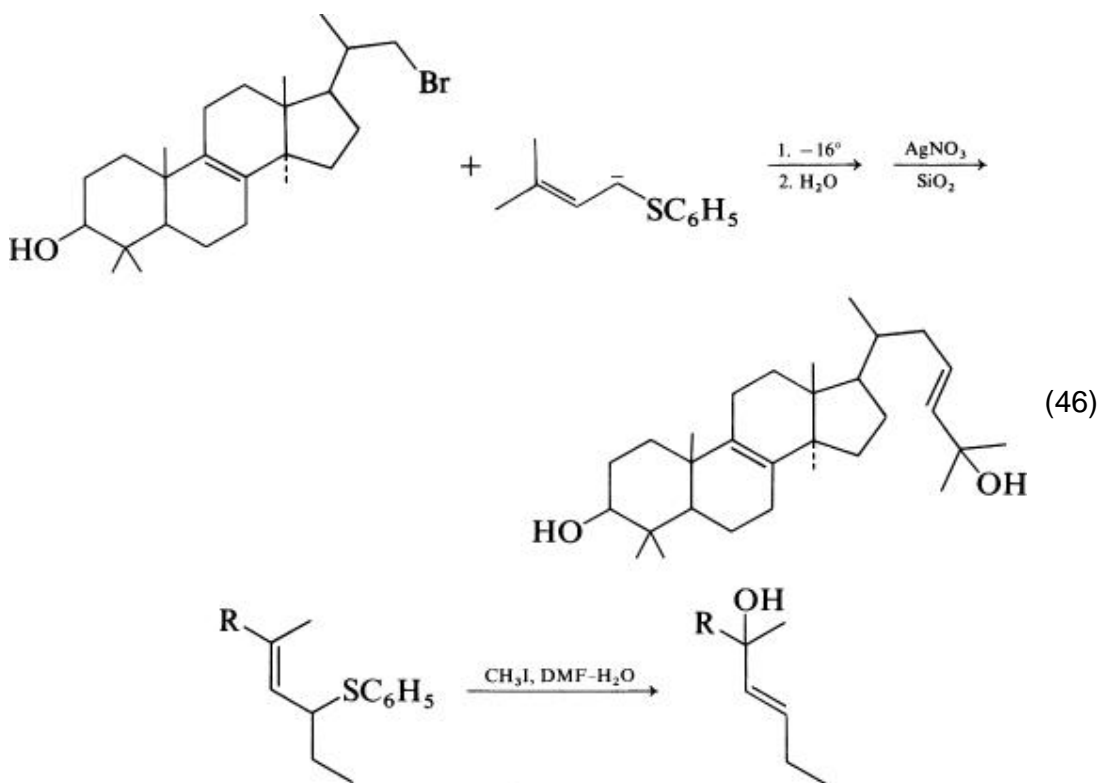
Sulfoxides and selenoxides undergo a [2,3]sigmatropic shift to sulfenates and selenates, respectively. By reduction or oxidation the latter can be changed into alcohols (Eq. 44). (144, 271, 307, 308)



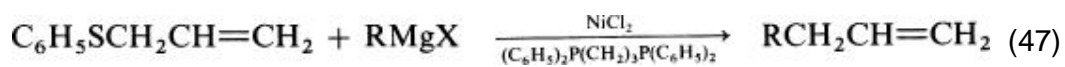
Propargyl selenoethers can be converted into  $\alpha$ ,  $\beta$ -unsaturated ketones (Eq. 45). (308a)



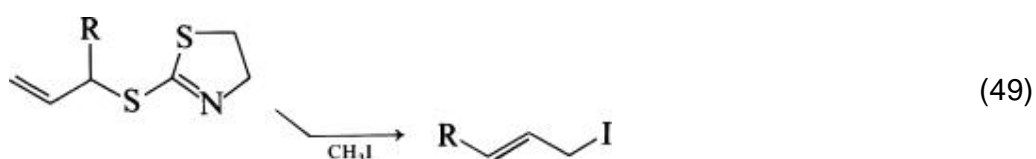
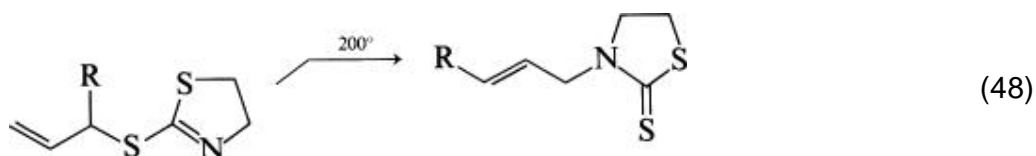
Displacements of sulfur in allylic thioethers can be achieved either by treatment with silica gel impregnated with silver nitrate or by treatment with methyl iodide in dimethylformamide–water (Eq. 46). (309, 310)



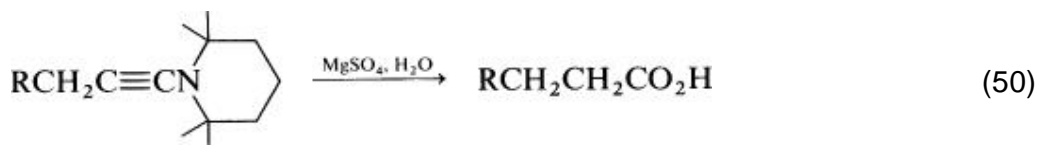
The thiophenyl group in an allyl phenyl thioether is displaced by a Grignard reagent in the presence of a nickel–phosphine complex (Eq. 47). (310a)

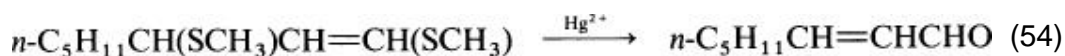
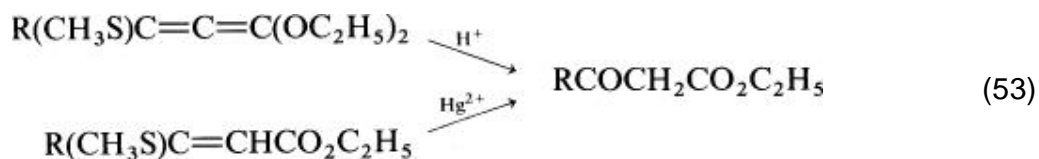


Allylic thiothiazolines can be converted to amines by thermal rearrangement (Eq. 48) (311) and to allyl iodides by treatment with methyl iodide (Eq. 49). (270, 311)



The hydrolysis of enamines, vinylic ethers and thioethers, cyanohydrin ethers, ketene ketals, and ynamines to aldehydes, ketones, acids, esters, and other derivatives proceeds by catalysis with acid or mercuric salts (Eqs. 50–54). (20, 33, 105, 124, 136, 137, 264, 265, 282, 312-314)

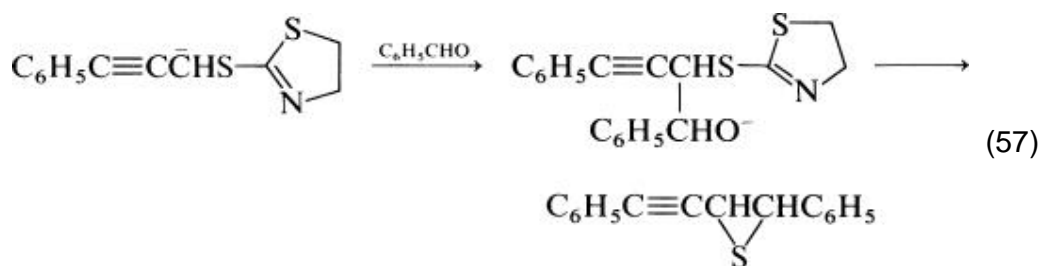
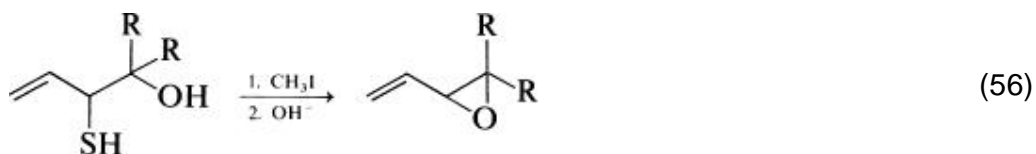




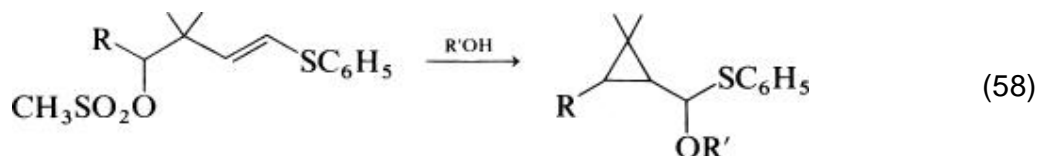
The thio Claisen rearrangement with desulfurization yields a  $\gamma$ ,  $\delta$ -unsaturated aldehyde (Eq. 55). (129)



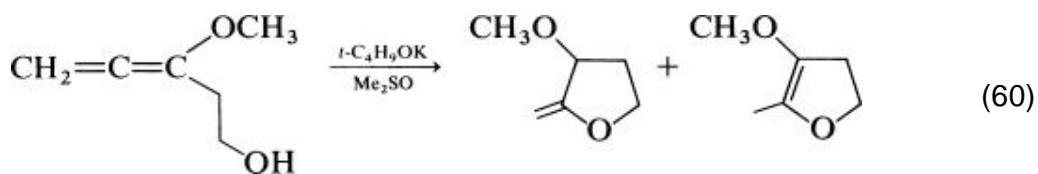
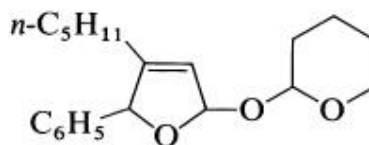
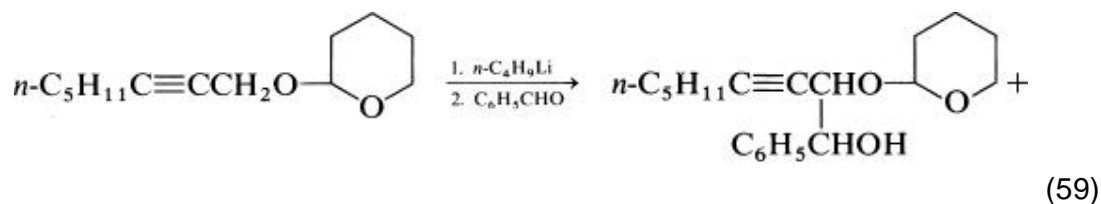
Epoxides and episulfides are obtained as the reaction products of carbanions derived from allylic thioethers (Eq. 56) and carbonyl compounds (Eq. 57). (267, 311)



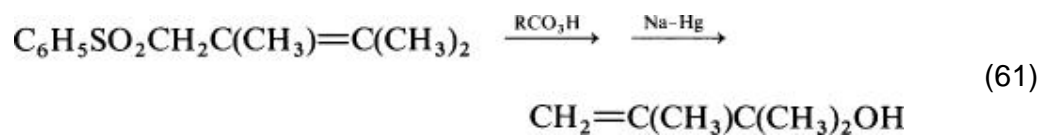
Solvolytic cyclization to a cyclopropane is observed with a mesylate (Eq. 58). (315)



The condensation products of carbanions from propargylic ethers with ethylene oxide and carbonyl compounds cyclize to dihydrofurans spontaneously (Eq. 59) or in the presence of base (Eq. 60). (30, 316)

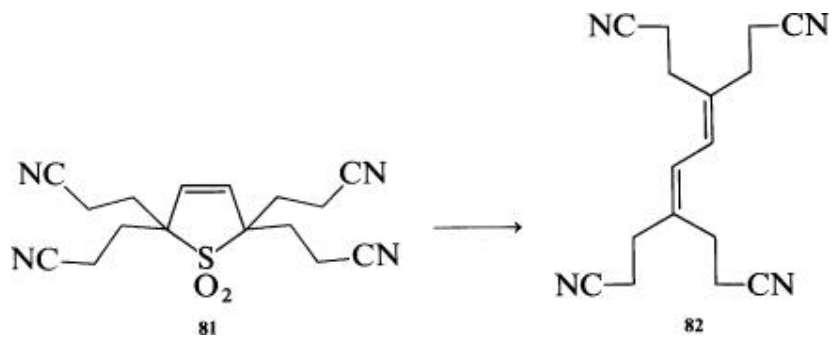


Epoxidation of the double bond may lead to new structural elements. The reaction product of allyltrimethylsilane carbanion with a ketone can be transformed into a substituted butyrolactone, (284c) and an allyl aryl sulfone to an allylic alcohol (Eq. 61). (316a)



Thermal extrusion of sulfur dioxide from sulfolene **81** leads to the diene **82**. (156)





Further transformations of the products derived from carbanions of isonitriles are described in a review. (317)

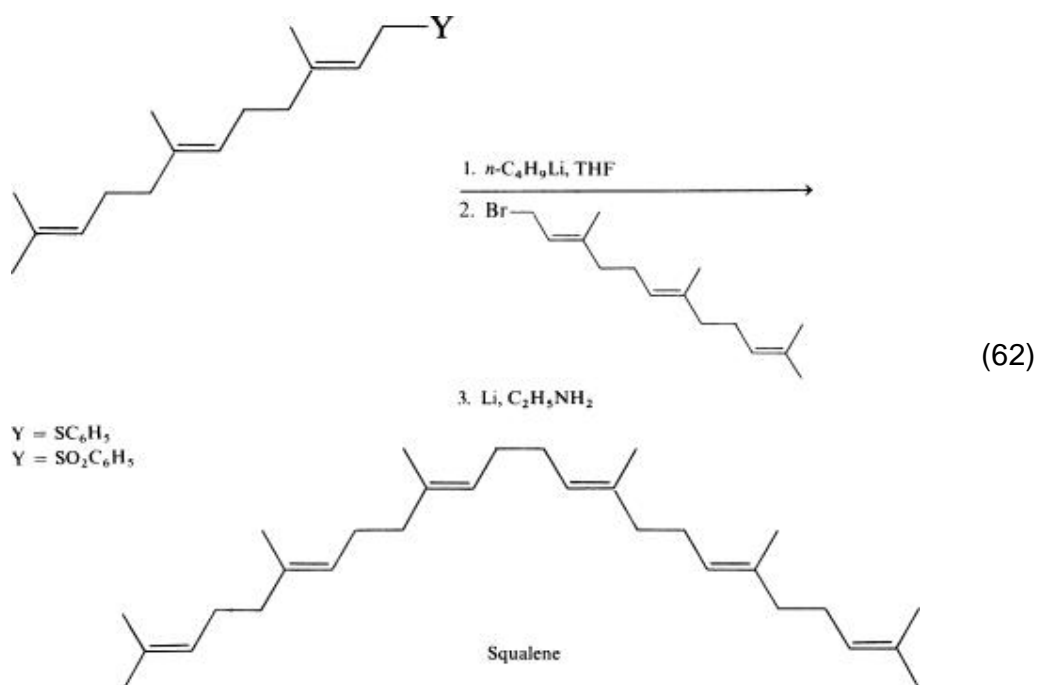
The ability to transform boranes to various functional groups makes it attractive to study carbanions derived from boranes. (318)

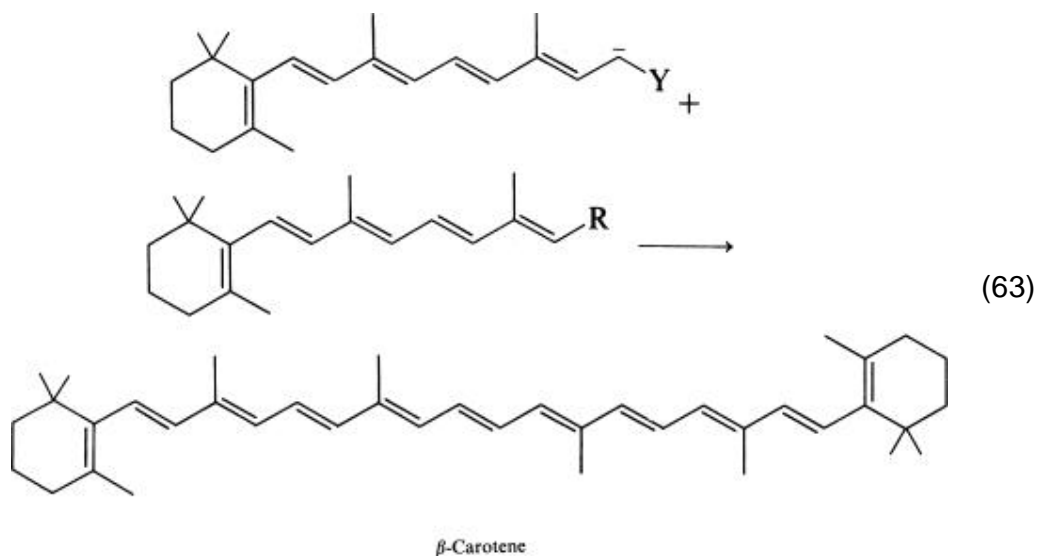
## 9. Applications

In this section we wish to illustrate the use of the heterosubstituted allylic carbanions in organic synthesis. We have selected only a few examples. It is most likely that because of the continuous developments in this field numerous new procedures will be added in the future.

The most important developments have occurred in the field of terpene synthesis. Activating groups Y linked to isoprenoid units can give rise to a carbanion that is alkylated with an isoprenoid halogenide. The activating group can then be removed either by reduction or by elimination.

The syntheses of squalene (Eq. 62), (87, 319) (*R*)- and (*S*)-squalene epoxide, (320) as well as analogs, (226, 321) and  $\beta$ -carotene (Eq. 63) illustrate this approach.

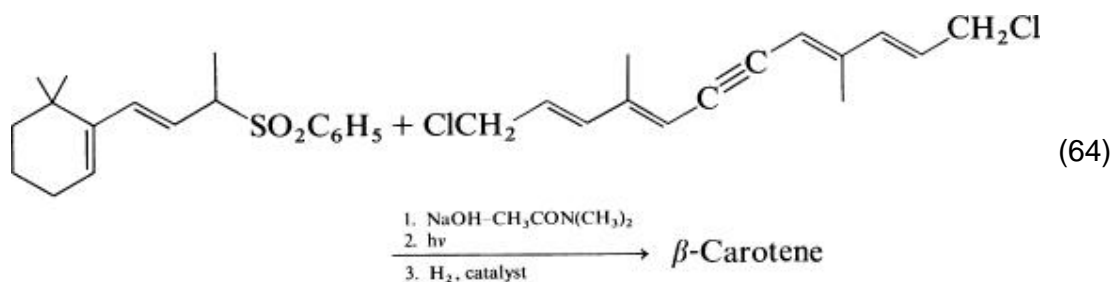




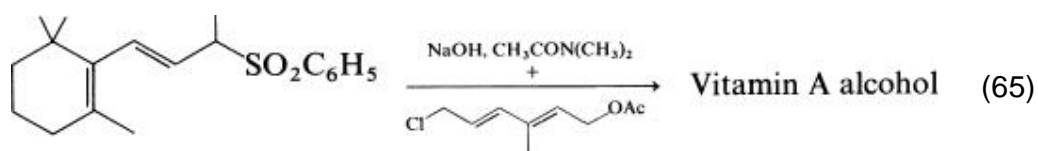
The synthesis of  $\beta$ -carotene was achieved using the following:

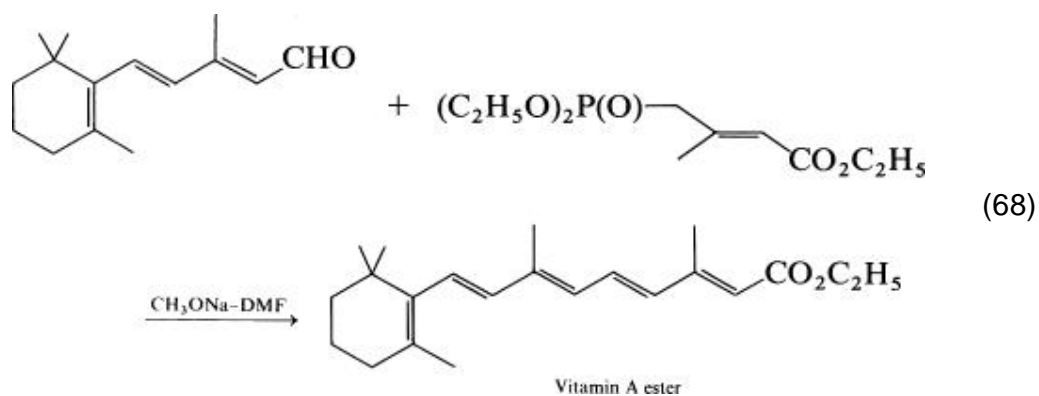
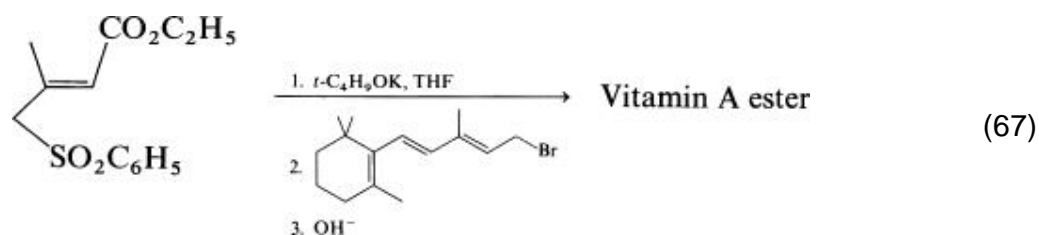
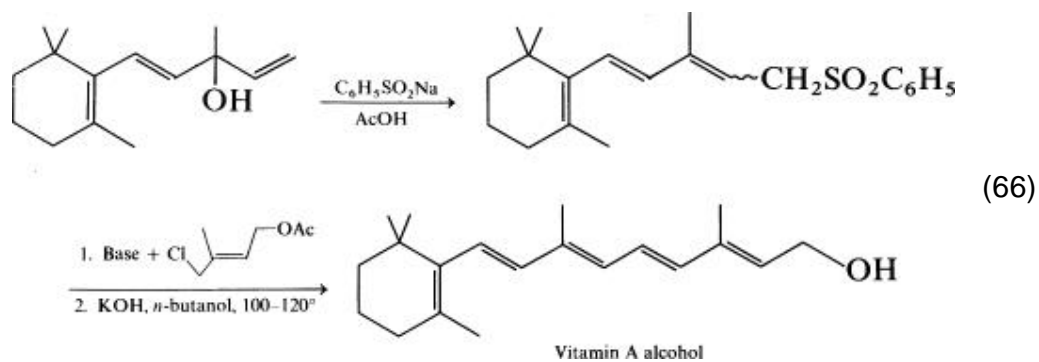
1. an isonitrile as an activating group ( $Y = \text{NC}$ ) and condensing the carbanion with the aldehyde  $R = \text{CHO}$  (245) and
2. a phenyl sulfone ( $Y = \text{SO}_2\text{C}_6\text{H}_5$ ) and condensing the carbanion with a chloride or a bromide ( $R = \text{CH}_2\text{Cl}$  or  $\text{CH}_2\text{Br}$ ). The phenylsulfonyl group was eliminated by treatment with base (Eq. 63). (322)

Ways of building the  $\text{C}_{40}$  carotene skeleton other than  $\text{C}_{20}$  coupling are  $\text{C}_{20-n} + \text{C}_{2n} + \text{C}_{20-n}$  coupling using a phosphonate allylic anion (323) or a sulfonyl anion (Eq. 64). (324)

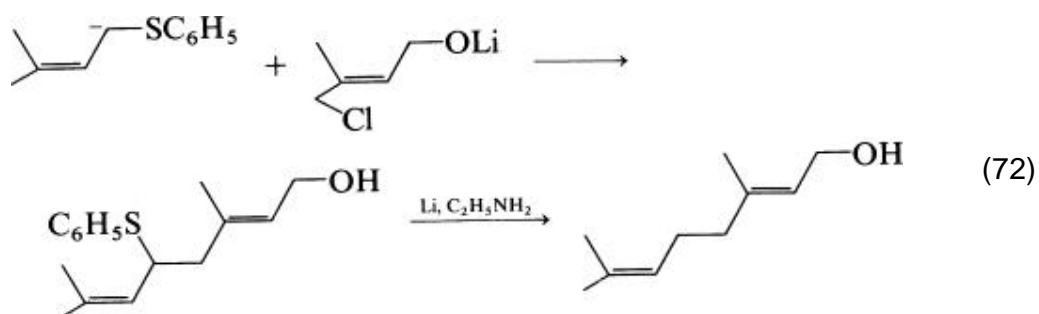
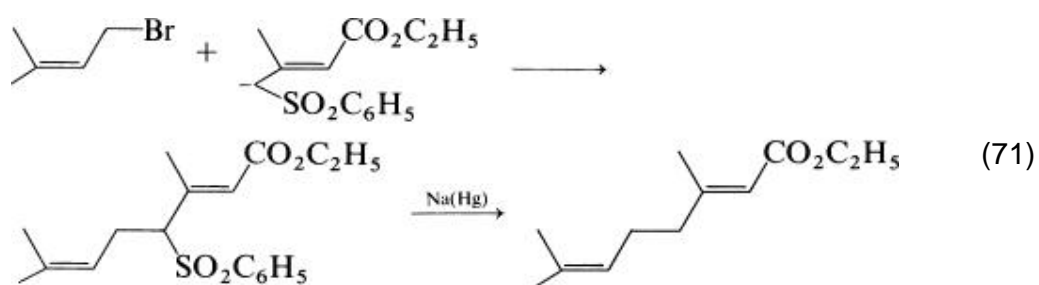
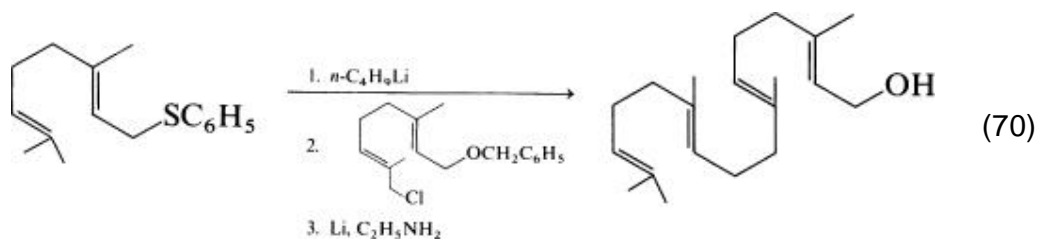
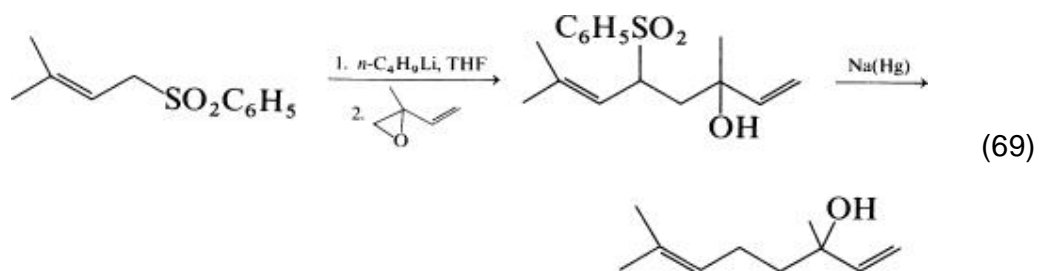


Vitamin A has been prepared as illustrated in Eqs. 65 and 66, (305, 306) and similar schemes exist for the corresponding ester (Eqs. 67 and 68). (184, 325)

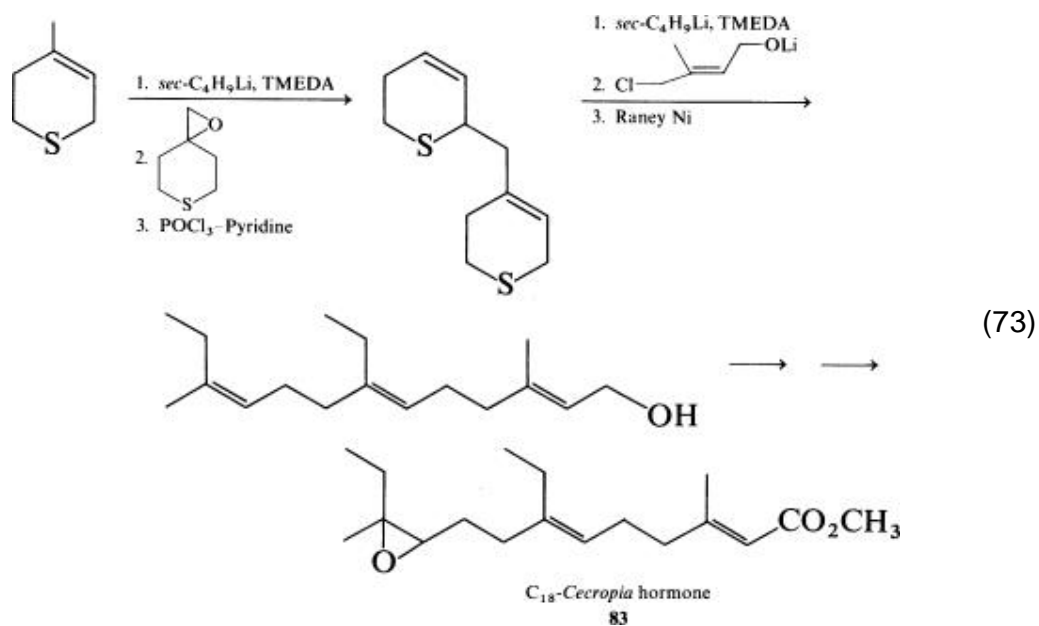




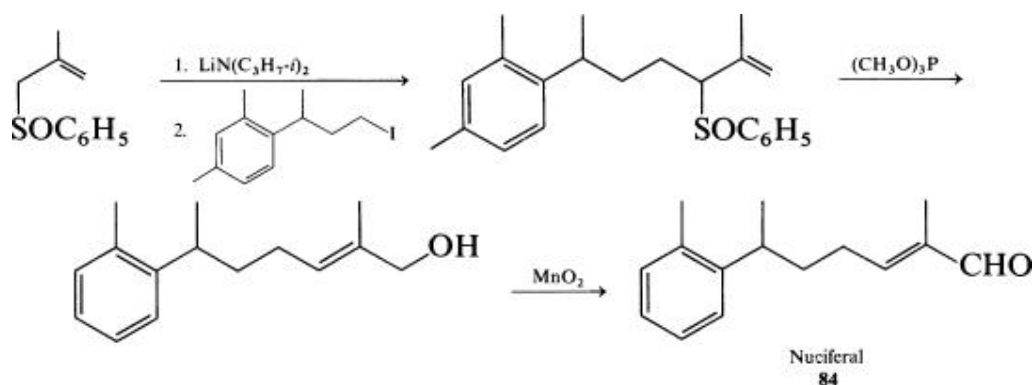
This method provides several elegant solutions to the problem of terpene homologation exemplified by the syntheses of linalol (Eq. 69), all-*trans* geranylgeraniol (Eq. 70), ethyl geraniate (Eq. 71), and geraniol (Eq. 72). (130, 147, 296, 326, 327)



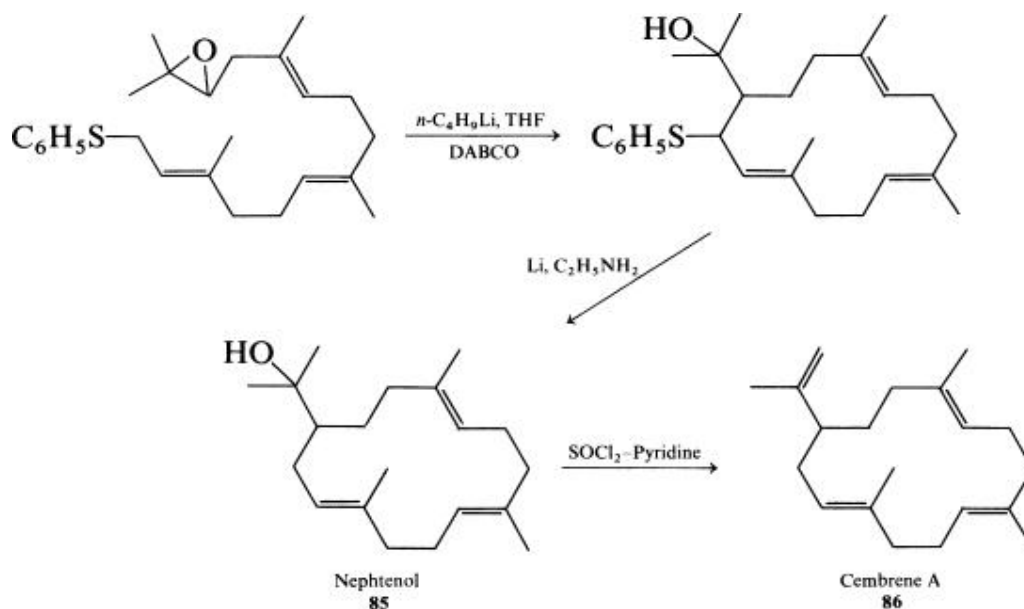
Several syntheses of *Cecropia* juvenile hormone **83** have used similar steps (Eq. 73). (130, 142, 143)



The synthesis of the sesquiterpenic aldehyde nuciferal **84** uses an allylic sulfoxide anion, the activating function being transformed into an allylic alcohol. (271)

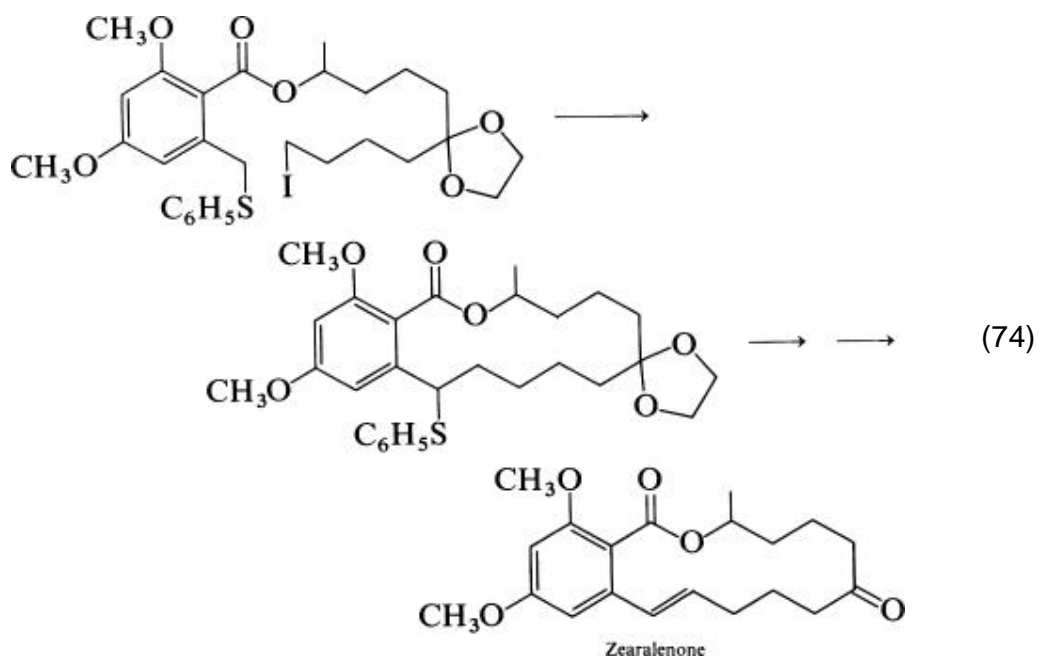


An efficient preparation of terpenes containing a large ring, as exemplified by naphthenol **85** and cembrene A (**86**), trail-marking pheromones of termites, employs an intramolecular cyclization of an anion with epoxide. (242)

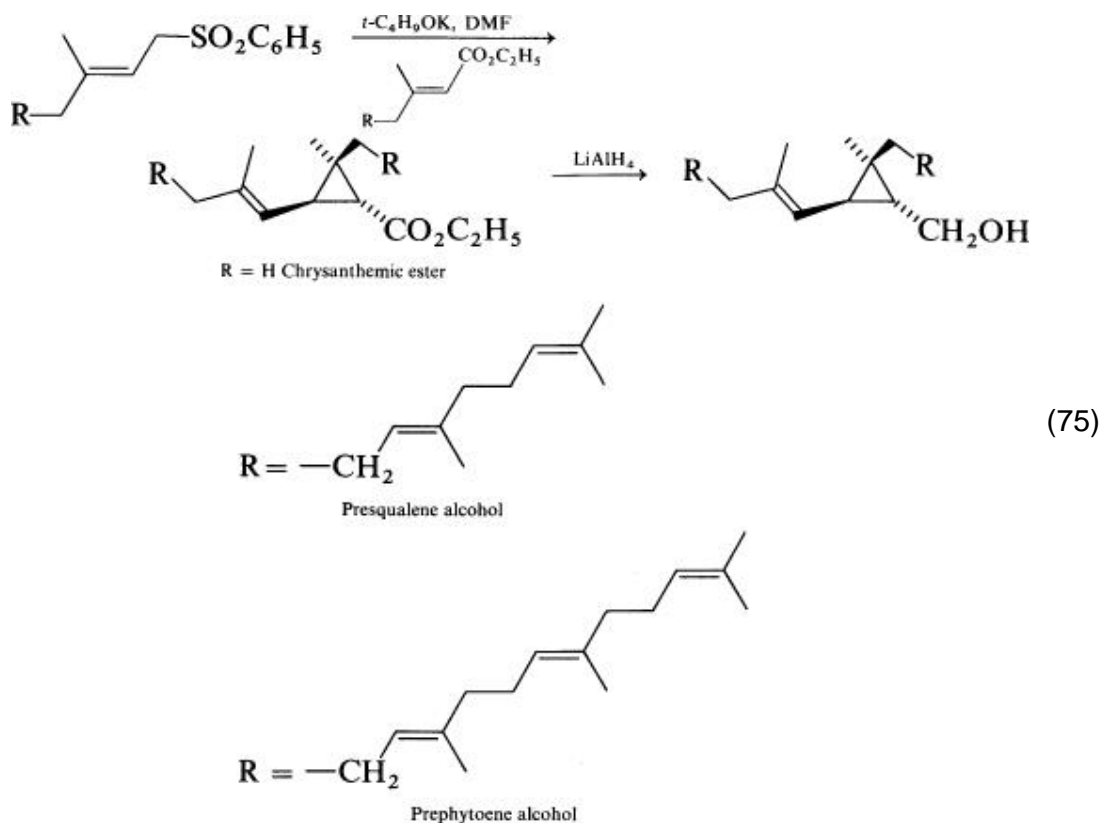


In contrast, the phenyl geranyl thioether epoxide leads to four- and five-membered ring systems. (327a)

An efficient intramolecular cyclization to a large ring has led to the synthesis of zearalenone. (327b) The ester group is likely shielded from inter-molecular reaction by the *ortho* methoxyl (Eq. 74).



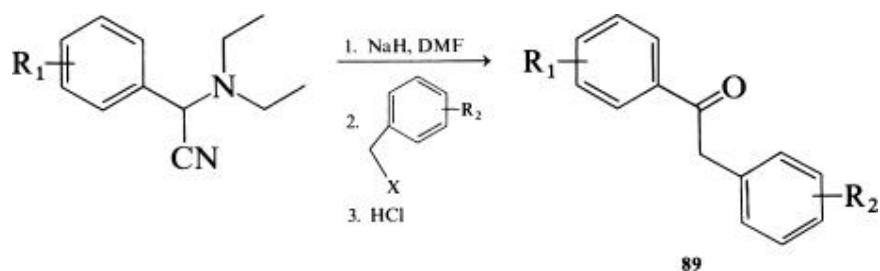
The formation of cyclopropanes by the condensation of carbanions derived from sulfones with  $\alpha, \beta$ -unsaturated esters has rather wide applications as in the synthesis of ( $\pm$ )-chrysanthemic ester, (145, 252) ( $\pm$ )-presqualene alcohol, (148) and ( $\pm$ )-prephytoene alcohol (Eq. 75). (328)



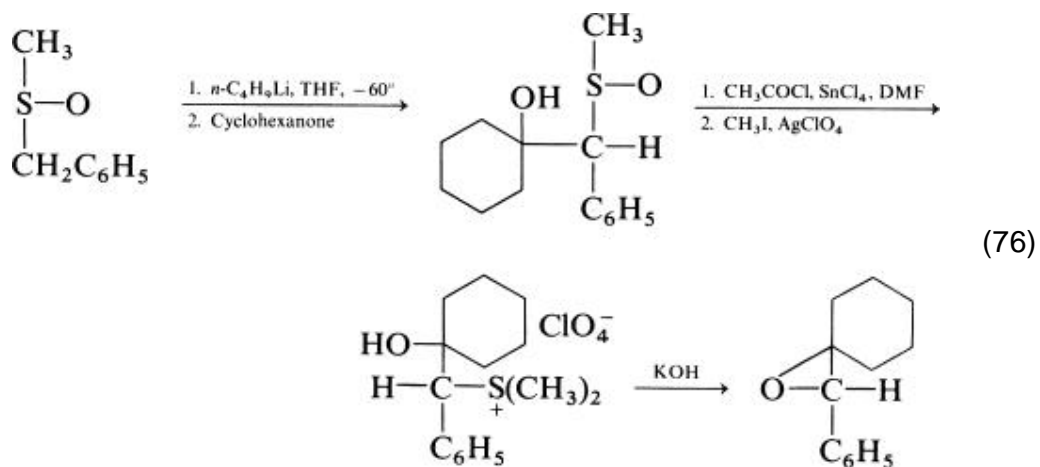
The preparation of the sex pheromones **87** of various insects uses the allylic rearrangement of an activating group so as to successively react both ends of the allylic system. (138)







The synthesis of optically active epoxides from  $\beta$ -hydroxy sulfoxides involves the use of the stereoselectivity of the carbanion alpha to the sulfoxides (Eq. 76). (331)



## 10. Experimental Considerations

The recommendations in this section should be followed in the procedures described below.

All glassware must be flame dried or dried in an oven at 120–150°. Argon or nitrogen is dried and freed from oxygen. The solvents, tetrahydrofuran, diethyl ether, and dimethoxyethane, of the best available grade, are dried first over molecular sieves and then distilled over lithium aluminum hydride or sodium benzophenone ketyl. It is preferable to avoid storage of dried solvents and to distill the solvents just before use. It is convenient, when using small volumes of anhydrous solvents, to have a distilling unit with continuous reflux where the solvent may be removed from the top through a stopcock or through a septum by means of a hypodermic syringe.

**Caution: Hexamethylphosphoramide should be handled in a hood with very good ventilation.**

*n*-Butyllithium in hexane as a commercial preparation may be used as such. The content is determined and the absence of halogen is checked by a silver nitrate reaction. *sec*-Butyllithium and *t*-butyllithium are also available from commercial firms and are of satisfactory quality for most uses. The *sec*-butyllithium may be prepared from *sec*-butyl bromide and lithium and purified by vacuum distillation. (126) **Solutions of lithium compounds in hydrocarbon solvents ignite in air and should be handled with care.** All reagents should be anhydrous and are often added as solutions in tetrahydrofuran. Tetramethylethylenediamine is distilled over calcium hydride: bp 121°.

## 11. Experimental Procedures

### 11.1.1.1. 2-Methyl-4-thiophenyl-2-pentene

(Metalation with *n*-butyllithium in the presence of 1,4-diazabicyclo[2.2.2]octane.) (82) To a solution of prenyl phenyl sulfide (1.2 g, 6.73 mmol) and 1,4-diazabicyclo[2.2.2]octane (0.9 g, 8 mmol) in tetrahydrofuran (20 mL) at  $-15^{\circ}$  was added dropwise with stirring *n*-butyllithium (8 mmol) (2 M commercial preparation in hexane). The orange-red mixture was stirred 30 minutes at  $-15^{\circ}$  before methyl iodide (0.5 mL) was added. The orange-red color was discharged instantaneously, the mixture was poured into water and extracted with ether, and the organic phase dried over sodium sulfate. Concentration under reduced pressure afforded 1.28 g (99%) of 2-methyl-4-thiophenyl-2-pentene (99% pure by glpc); nmr (CDCl<sub>3</sub>)  $\delta$  (ppm): 1.31 (d, 3 H,  $J = 6.5$  Hz), 1.38 (d, 3 H,  $J = 1.5$  Hz), 1.63 (d, 3 H,  $J = 1.5$  Hz), 4.00 (d of q, 1 H,  $J = 6.5$  and 9.5 Hz), 6.00 (d, 1 H,  $J = 9.5$  Hz), and 7.16–7.55 (m, 5 H); mass spectrum  $m/e$ : 192 ( $M^+$ ) and 109 (base).

### 11.1.1.2. 3-(1'-Vinyl-1'-cyclohexyl)-thioisopropyl-1-propene

(Metalation with *n*-butyllithium and addition of cuprous iodide.) (283) To a solution of allyl isopropyl thioether (2.35 g, 20 mmol) in dry ether (70 mL) was added with stirring at  $-78^{\circ}$  *sec*-butyllithium (20 mmol) (1.02 M solution in pentane). The mixture was warmed to  $-25^{\circ}$  for 30 minutes, recooled to  $-78^{\circ}$ , and treated with cuprous iodide (4.95 g, 26 mmol), after which a white suspension formed. The mixture was then stirred for 15 minutes at  $-78^{\circ}$  and 2-cyclohexylidene-1-bromoethane (1.90 g, 10 mmol) was added. The suspension, which became dark after 10 minutes, was kept for 4 hours at  $-78^{\circ}$  and then partitioned between dilute hydrochloric acid and ether. The organic phase was washed with water, dried, and freed of solvent. The remaining pale-yellow liquid was subjected to column chromatography (silica gel, 100 g) with *n*-hexane as an eluant to yield 3-(1'-vinyl-1'-cyclohexyl)-1-thioisopropyl-1-propene (2.07 g, 97%), bp  $145^{\circ}$  (3 mm); ir (neat)  $\text{cm}^{-1}$ : 1640 (CH = CHS), 1612, 1000, 945, and 913 (CH<sub>2</sub> = CH); nmr (CCl<sub>4</sub>)  $\delta$  (ppm): 1.25 (d, 6 H,  $J = 7$  Hz), 1.40 (broad s), 2.03 (d, 2 H,  $J = 7$  Hz), 3.00 (d of q, 1 H,  $J = 7$  and 7 Hz), 4.96 (d of d, 1 H,  $J = 2$  and 17 Hz), 5.09 (d of d, 1 H,  $J = 2$  and 12 Hz), 5.60 (d of t, 1 H,  $J = 7$  and 15 Hz), 5.70 (d of d, 1 H,  $J = 12$  and 17 Hz), and 6.02 (d, 1 H,  $J = 15$  Hz).

### 11.1.1.3. (E)-1-*N,N*-Dimethyldithiocarbamate-2-pentene

(Metalation with lithium diisopropylamine.) (138) *n*-Butyllithium (24 mmol) (2 M commercial preparation in hexane) was added at  $-55^{\circ}$  to a solution of *S*-allyl-*N,N*-dimethyldithiocarbamate (3.55 g, 22 mmol) and diisopropylamine (3 g, 29 mmol) in tetrahydrofuran (volume not given). To the resulting deep-red solution was added (below  $-55^{\circ}$ ) a solution of ethyl iodide (4.26 g, 30 mmol) in

tetrahydrofuran (5 mL) and the solution was stirred. After 15 minutes the red color had completely disappeared. The solution was washed with 20% aqueous ammonium chloride, acidified with dilute hydrochloric acid, and again washed with 20% aqueous ammonium chloride. The solvent was removed and the product refluxed in chloroform (40 mL) for 3 hours. Distillation under reduced pressure afforded (*E*)-(1-*N,N*-dimethyldithiocarbamate)-2-pentene (93%), bp 117–121° (3.5 mm); ir  $\text{cm}^{-1}$ : 1500, 1258, 1150 [ $\text{C}(\text{S})\text{N}(\text{CH}_3)_2$ ], and 970 ( $\text{CH} = \text{CH}$ ); nmr  $\delta$  (ppm): 1.00 (t, 1 H), 3.40 (s, 3 H), 3.54 (s, 3 H), 3.94 (d, 2 H), 5.51, and 5.73 (d of t, 2 H,  $J = 15.3$  Hz).

#### 11.1.1.4. (*Z*)-1-Butenyl Phenyl Ether

(*Metalation by potassium *t*-butoxide-*n*-butyllithium.*) (89) To a suspension of potassium *t*-butoxide (11.8 g, 105 mmol) in petroleum ether (200 mL) and allyl phenyl ether (13.4 g, 100 mmol) was added dropwise over 20 minutes at  $-30^\circ$  *n*-butyllithium (105 mmol) (1.6 *M* in hexane solution). The mixture was kept for 1 hour at  $-30^\circ$  and then treated with methyl iodide (15.6 g, 110 mmol) so as to discharge the red color. Analysis by gas chromatography (20% SE 30, 2 m column, 100 or 180° within 8 minutes) showed that a mixture of (*Z*)-1-butenyl phenyl ether (44%), but-1-en-3-yl phenyl ether (16%), (*Z*)-1-heptenyl phenyl ether (13%), and hept-1-en-3-yl phenyl ether (2%) was obtained. Water was added, the organic layer was washed three times with 50 mL of water, dried, concentrated with a Widmer column, and distilled to afford 12.3 g of a liquid, bp 93–95° (14 mm). The pure components were obtained by glpc (15% Apiezon L, 6 m column, 166°). (*Z*)-1-Butenyl phenyl ether, ir (film)  $\text{cm}^{-1}$ : 1670 ( $\text{C} = \text{C}$ ) and 1240 ( $\text{C} - \text{O}$ ); nmr  $\delta$  (ppm): 1.00 (t, 3 H,  $J = 7.5$  Hz), 2.23 (d, 2 H,  $J = 7.5$  Hz), 4.75 (q, 1 H,  $J = 7$  Hz), 6.26 (d, 1 H,  $J = 6$  Hz), and 7.0 (m, 5 H); mass spectrum  $m/e$ : 148 ( $\text{M}^+$ ) and 94 (base). But-en-3-yl phenyl ether, ir (film)  $\text{cm}^{-1}$ : 1660 ( $\text{C} = \text{C}$ ), 1240 ( $\text{C} - \text{O}$ ), 990, and 925 ( $\text{CH} = \text{CH}_2$ ); nmr  $\delta$  (ppm): 1.38 (d, 3 H,  $J = 6.5$  Hz), 4.72 (d, 1 H,  $J = 6.5$  Hz), 5.22, 5.70 (2 m, 3 H), and 7.0 (m, 5 H); mass spectrum  $m/e$ : 148 ( $\text{M}^+$ ) and 94 (base). Hept-1-en-yl phenyl ether, ir (film)  $\text{cm}^{-1}$ : 1670 ( $\text{C} = \text{C}$ ) and 1240 ( $\text{C} - \text{O}$ ); nmr  $\delta$  (ppm): 0.90 (t, 3 H,  $J = 7$  Hz), 1.4 (m, 6 H), 2.20 (q, 2 H,  $J = 7$  Hz), 4.75 (q, 1 H,  $J = 7$  Hz), 6.29 (d, 1 H,  $J = 7$  Hz), and 7.0 (m, 5 H); mass spectrum  $m/e$ : 190 ( $\text{M}^+$ ) and 94 (base). Hept-1-en-3-yl phenyl ether, ir (film)  $\text{cm}^{-1}$ : 1240 ( $\text{C} - \text{O}$ ), 990, and 903 ( $\text{CH} = \text{CH}_2$ ); nmr  $\delta$  (ppm): 0.92 (t, 3 H,  $J = 7$  Hz), 1.5 (m, 6 H), 4.53 (q, 1 H,  $J = 6$  Hz), 5.2, 5.7 (2 m, 3 H), and 7.0 (m, 5 H); mass spectrum  $m/e$ : 190 ( $\text{M}^+$ ) and 94 (base).

#### 11.1.1.5. 2,7-Dimethyl-4-Phenylsulfonyl-2,6-octadiene

(*Metalation with potassium *t*-butoxide.*) (332) To a suspension of potassium *t*-butoxide (1.88 g, 16.8 mmol) in tetrahydrofuran (3 mL) was added at  $-10^\circ$  over 2 minutes phenyl 3-methyl-2-butenyl sulfone (1.05 g, 5 mmol) in tetrahydrofuran (4 mL). Isoprenyl chloride (0.83 g, 8 mmol) in tetrahydrofuran (2 mL) was then added during 4 minutes. The mixture was stirred for 1.25 hours at  $-10^\circ$ , 1 hour at  $0^\circ$ , and 2 hours at  $18^\circ$ , then poured into water (25 mL) and extracted with diethyl ether. The ethereal extract was dried over

magnesium sulfate and concentrated under reduced pressure to afford 1.38 g of 2,7-dimethyl-4-phenylsulfonyl-2,6-octadiene (99%) as a pale-yellow oil; nmr (CCl<sub>4</sub>) δ (ppm): 1.21 (s, 3 H), 1.63 (s, 6 H), 1.70 (s, 3 H), 2–3.06 (m, 2 H), 3.56 (d of t, *J* = 4 and 10 Hz), 4.83 (m, 1 H), 5.0 (m, 1 H), and 7.43–7.90 (m, 5 H).

#### 11.1.1.6. Ethyl α -Isocyanophenylacetate

(*Metallation with sodium hydride*). (152) A mixture of benzyl isocyanide (2.34 g, 20 mmol) and diethyl carbonate (2.36 g, 20 mmol) in dimethylformamide (10 mL) was gradually added to a suspension of sodium hydride (0.84 g, 22 mmol, 63% in oil) in dimethylformamide (15 mL) at 15° for 15 minutes under stirring. After 1 hour the reaction mixture was neutralized with acetic acid while cooling with an ice bath and the solvent was removed under reduced pressure below 50°. The residue was extracted with ethyl acetate and the extract washed with water and dried over magnesium sulfate. The solvent was evaporated under reduced pressure and the product purified by column chromatography on silica gel (80 g, kieselgel 0.2–0.5 mm, E. Merck). The paraffin present in the sodium hydride was removed by elution with *n*-hexane, and ethyl α -isocyanophenylacetate (2.38 g) was eluted with benzene (63% yield); ir (neat) cm<sup>-1</sup>: 2130 (NC) and 1752 (CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>); nmr (CCl<sub>4</sub>) δ (ppm): 1.23 (t, 3 H), 4.18 (q, 2 H), 5.22 (s, 1 H), and 7.40 (s, 5 H).

## 12. Tabular Survey

The following tables contain examples where heterosubstituted allylic and benzylic carbanions were intermediates in an organic synthesis. The literature has been consulted to December 1979. The compounds are arranged according to their functionality, then in order of increasing carbon atoms.

Abbreviations are as follows:

[2.2.2]	1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo-[8.8.8]-hexacosane, ([2.2.2]cryptand)
9-BBN	9-borabicyclo[3.3.1]nonane
cat	catalytic
DABCO	1,4-diazabicyclo[2.2.2]octane
DDB	1,4-dimethylamino-2,3-dimethoxybutane
Diglyme	bis(2-methoxyethyl) ether
eq	equivalent
ether	diethyl ether
Hydrolysis conditions or reagents not given in the publication	
LDA	lithium diisopropylamide
LICA	lithium isopropylcyclohexyl amide
Liq	liquid
LTMP	lithium 2,2,6,6-tetramethylpiperidide
THF	tetrahydrofuran
THP	2-tetrahydropyranyl
TMEDA	N,N,N',N'-tetramethylethylenediamine
Ts	<i>p</i> -toluenesulfonate

## 13. Acknowledgment

We acknowledge the help of Mrs. D. Voegel who typed the manuscript. A major part of this chapter was written at the Centre Nicolas Grillet, Rhône-Poulenc Industries, Vitry-sur-Seine, France.

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### Table I. Amides

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### Table II. Amines

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### Table III. Boranes

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### Table IV. Bromides

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### Table V. Chlorides

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**Table VI. Cyanohydrin Ethers**

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**Table VII. Dithiocarbamates**

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**Table VIII. Dithioesters**

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**Table IX. Dithioketals**

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**Table X. Ethers**

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**Table XI. Hemithioketals**

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**Table XII. Iminodithiocarbonate Diesters**

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**Table XIII. Isonitriles**

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**Table XIV. Ketals**

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**Table XV. Nitro Derivatives**

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**Table XVI. Nitrosoamines**

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**Table XVII. Phosphates**

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**Table XVIII. Phosphinamides**

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**Table XIX. Phosphinates**

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**Table XX. Phosphine Oxides**

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**Table XXI. Phosphine Sulfides**

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**Table XXII. Phosphinothioates**

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**Table XXIII. Phosphonamides**

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**Table XXIV. Phosphonates**

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**Table XXV. Phosphinodithioates**

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**Table XXVI. Phosphoramides**

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**Table XXVII. Selenides**

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**Table XXVIII. Selenoxides**

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**Table XXIX. Silanes**

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**Table XXX. Sulfines**

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**Table XXXI. Sulfonamides**

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**Table XXXII. Sulfones**

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**Table XXXIII. Sulfonic Esters**

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**Table XXXIV. Sulfoxides**

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**Table XXXV. Sulfoximines**

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**Table XXXVI. Tellurides**

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**Table XXXVII. Thiocarbamates**

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**Table XXXVIII. Thioethers**

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**Table XXXIX. Thioisonitriles**

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**Table XL. Thioketones**

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**Table XLI. Thiols**

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**Table XLII. Thiophosphinates**

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TABLE I. AMIDES

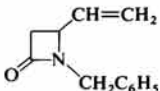
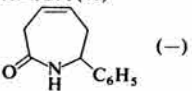
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> CONHCH <sub>2</sub> CH=CH <sub>2</sub>	LDA (2 eq), diglyme, -78°	H <sub>2</sub> O	<i>t</i> -C <sub>4</sub> H <sub>9</sub> CONHCH=CHCH <sub>2</sub> R A, R = H (78)	135c
C <sub>9</sub>	CH <sub>3</sub> O <sub>2</sub> CC(NCO)=C=CHSi(CH <sub>3</sub> ) <sub>3</sub>	LDA (excess), THF, -78°	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I, H <sub>2</sub> O C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (85) CH <sub>3</sub> O <sub>2</sub> CC(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )[NHCON(C <sub>3</sub> H <sub>7</sub> - <i>t</i> ) <sub>2</sub> ]C≡CSi(CH <sub>3</sub> ) <sub>3</sub> (-)	612
C <sub>10</sub>	C <sub>6</sub> H <sub>5</sub> CONHCH <sub>2</sub> CH=CH <sub>2</sub>	LDA (2 eq), diglyme, -78°	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CONHCH=CHCH <sub>2</sub> R A, R = H (83)	135c
C <sub>11</sub>	C <sub>6</sub> H <sub>5</sub> CONHCH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub>	LDA (2 eq), diglyme, -78°	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I, H <sub>2</sub> O H <sub>2</sub> O	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (91) C <sub>6</sub> H <sub>5</sub> CONHCH=C(CH <sub>3</sub> )CH <sub>2</sub> R A, R = H (90)	135c
	(CH <sub>3</sub> ) <sub>3</sub> SiC≡CCH(CO <sub>2</sub> CH <sub>3</sub> )NHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	LDA, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, THF, -70°, 15 min	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I, H <sub>2</sub> O CH <sub>2</sub> =CHCH <sub>2</sub> Br, -70°, 3 hr	(CH <sub>3</sub> ) <sub>3</sub> SiC≡CC(R)(CO <sub>2</sub> CH <sub>3</sub> )(NHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) A, R = CH <sub>2</sub> =CHCH <sub>2</sub> (70)	613
	<i>t</i> -C <sub>4</sub> H <sub>9</sub> CONHCH <sub>2</sub> C≡CSi(CH <sub>3</sub> ) <sub>3</sub>	LDA or <i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -78°	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br CH <sub>2</sub> =CHCO <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> =CHCH <sub>2</sub> Br	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (60) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (75) A, R = CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> (65) <i>t</i> -C <sub>4</sub> H <sub>9</sub> CONHCH(R)C≡CSi(CH <sub>3</sub> ) <sub>3</sub> A, R = CH <sub>2</sub> =CHCH <sub>2</sub> (65)	613 613 613 613
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> I C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br CH <sub>2</sub> =CHCO <sub>2</sub> CH <sub>3</sub> CO <sub>2</sub> , then CH <sub>2</sub> N <sub>2</sub>	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (75) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (90) A, R = CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> (85) A, <i>t</i> -C <sub>4</sub> H <sub>9</sub> CONHCH(CO <sub>2</sub> CH <sub>3</sub> )C≡CSi(CH <sub>3</sub> ) <sub>3</sub> + B, <i>t</i> -C <sub>4</sub> H <sub>9</sub> CONHC(CO <sub>2</sub> CH <sub>3</sub> )=C=CSi(CH <sub>3</sub> ) <sub>3</sub> A: 4, B: 1 (40)	612 612 612 612
C <sub>12</sub>		LDA, THF, -78°	H <sub>2</sub> O	 (-)	196



TABLE I. AMIDES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
64 C <sub>12</sub> (Contd.)		LDA, THF, -78°	H <sub>2</sub> O	 (97)	196
C <sub>13</sub>		LDA, THF, -78°	H <sub>2</sub> O	A, B, A: 3, B: 2 (90)	196
C <sub>14</sub>	C <sub>6</sub> H <sub>5</sub> CONHCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	LDA (2 eq), diglyme, -78°	CH <sub>3</sub> I, H <sub>2</sub> O n-C <sub>4</sub> H <sub>9</sub> I, H <sub>2</sub> O C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl, H <sub>2</sub> O C <sub>6</sub> H <sub>5</sub> CHO, H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CONHCH(R)C <sub>6</sub> H <sub>5</sub> A, R = CH <sub>3</sub> (79) A, R = C <sub>4</sub> H <sub>9</sub> -n (95) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (79) A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (-)	135b 135b 135b 135b
		LDA, THF, -78°, 1 min	D <sub>2</sub> O	 (-)	196
		LDA, THF, -78°, warmed to room temperature	-	A, CH <sub>2</sub> =C(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub> CONHCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> + B, A: 1, B: 1 (90)	196
C <sub>16</sub>		LDA, THF, -78°	H <sub>2</sub> O	 (93)	196
	C <sub>6</sub> H <sub>5</sub> CONHCH <sub>2</sub> C(C <sub>6</sub> H <sub>5</sub> )=CH <sub>2</sub>	LDA (2 eq), diglyme, -78°	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CONHCH=C(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> R A, R = H (70) A, R = C <sub>4</sub> H <sub>9</sub> -n (75)	135c 135c
	C <sub>6</sub> H <sub>5</sub> CONHCH(C <sub>6</sub> H <sub>5</sub> )CH=CH <sub>2</sub>	LDA (2 eq), diglyme, -78°	n-C <sub>4</sub> H <sub>9</sub> I, H <sub>2</sub> O H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CONHC(C <sub>6</sub> H <sub>5</sub> )=CHCH <sub>2</sub> R A, R = H (99) A, R = C <sub>4</sub> H <sub>9</sub> -n (99)	135c 135c
65 C <sub>21</sub>		LDA, THF, -78°	H <sub>2</sub> O	 (92)	196
	C <sub>6</sub> H <sub>5</sub> CON(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	LDA, THF, -78°, 4 min	CH <sub>3</sub> I, -78°, 1 hr, then room temperature CO <sub>2</sub> , -78°, 10 min CH <sub>3</sub> COCH <sub>3</sub> , -78°, 1 hr (CH <sub>3</sub> CO) <sub>2</sub> O, -78°, 1 hr	C <sub>6</sub> H <sub>5</sub> CON(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (81) C <sub>6</sub> H <sub>5</sub> CON(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )CH(CO <sub>2</sub> H)C <sub>6</sub> H <sub>5</sub> (98) C <sub>6</sub> H <sub>5</sub> CON(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )CH[C(OH)(CH <sub>3</sub> ) <sub>2</sub> ]C <sub>6</sub> H <sub>5</sub> (90) C <sub>6</sub> H <sub>5</sub> CON(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )CH(C <sub>6</sub> H <sub>5</sub> )COCH <sub>3</sub> (66)	25 25 25 25

TABLE II. AMINES


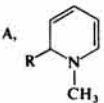
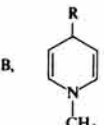


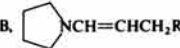
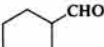
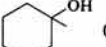
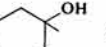
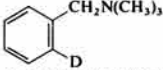

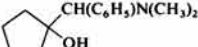
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>3</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> NH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (3 eq), <i>n</i> -C <sub>6</sub> H <sub>14</sub> , reflux	Hydrolysis	<i>n</i> -C <sub>6</sub> H <sub>13</sub> COC <sub>4</sub> H <sub>9</sub> - <i>n</i> (30)	551
C <sub>6</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>n</i> -C <sub>5</sub> H <sub>12</sub> , -50°	CH <sub>3</sub> I	A,  + B, 	132a 132a
C <sub>7</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (3 eq), <i>n</i> -C <sub>6</sub> H <sub>14</sub> , reflux	(CH <sub>3</sub> ) <sub>3</sub> SiCl Hydrolysis	A: 1, B: 1, R = CH <sub>3</sub> (55) A: 0, B: 100, R = Si(CH <sub>3</sub> ) <sub>3</sub> (6) C <sub>6</sub> H <sub>5</sub> COC <sub>4</sub> H <sub>9</sub> - <i>n</i> , (20)	411
	(CH <sub>3</sub> ) <sub>2</sub> C=C(CN)N(CH <sub>3</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, low temperature	CH <sub>3</sub> I	A, C <sub>2</sub> H <sub>5</sub> (CH <sub>3</sub> )C=C(CN)N(CH <sub>3</sub> ) <sub>2</sub> + B, CH <sub>2</sub> =C(CH <sub>3</sub> )C(CN)(CH <sub>3</sub> )N(CH <sub>3</sub> ) <sub>2</sub>	20 20
	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC≡CCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, ether, 0°, 5.5 hr	(CH <sub>3</sub> ) <sub>3</sub> SiCl, 0°, 14 hr CH <sub>2</sub> =CHCH <sub>2</sub> Br, -40°, 0.5 hr	A: 9, B: 1 (-) (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC≡CCH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub> (57) (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC(CH <sub>2</sub> CH=CH <sub>2</sub> )=C=CH <sub>2</sub> unstable (-)	614 614
		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, -78° then -10°, 2 hr	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br (0.8 eq), -78°, then room temperature, 1 hr  (CH <sub>3</sub> ) <sub>3</sub> SiCl	A,  + B, 	614 614
				A: 50, B: 50, R =  (64) A: 46, B: 54, R = C <sub>6</sub> H <sub>5</sub> CH(OH) (48) A: 43, B: 57, R = (CH <sub>3</sub> ) <sub>2</sub> C(OH) (59) A: 40, B: 60, R = C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )OH (74)	614 614 614
				A: 45, B: 55, R =  (71)	614
		ZnCl <sub>2</sub> added		A: 5, B: 95, R =  (42)	614
C <sub>8</sub>	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )NH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (3 eq), <i>n</i> -C <sub>6</sub> H <sub>14</sub> , reflux	Hydrolysis	<i>n</i> -C <sub>4</sub> H <sub>9</sub> C(C <sub>6</sub> H <sub>5</sub> )(CH <sub>3</sub> )NH <sub>2</sub> (25) + C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> (6) + C <sub>6</sub> H <sub>5</sub> COC <sub>4</sub> H <sub>9</sub> - <i>n</i> (6) + <i>n</i> -C <sub>4</sub> H <sub>9</sub> COC <sub>4</sub> H <sub>9</sub> - <i>n</i> (30)	551
C <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, 25°, 24 hr	D <sub>2</sub> O	 (0.94 D)	448
		C <sub>6</sub> H <sub>5</sub> Li, C <sub>6</sub> H <sub>6</sub> , <i>n</i> -C <sub>8</sub> H <sub>18</sub> , reflux 2 hr	C <sub>6</sub> H <sub>5</sub> CHO, ether, room temperature, 2 hr	C <sub>6</sub> H <sub>5</sub> CH(OH)CH(C <sub>6</sub> H <sub>5</sub> )N(CH <sub>3</sub> ) <sub>2</sub> (79) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> (18)	544
		C <sub>6</sub> H <sub>5</sub> NCO, ether, room temperature, 5 hr	C <sub>6</sub> H <sub>5</sub> NCO, ether, room temperature, 5 hr	C <sub>6</sub> H <sub>5</sub> NHCOCH(C <sub>6</sub> H <sub>5</sub> )N(CH <sub>3</sub> ) <sub>2</sub> (66)	544
		C <sub>6</sub> H <sub>5</sub> CN, C <sub>6</sub> H <sub>6</sub> , room temperature, 3 hr, then hydrolysis	C <sub>6</sub> H <sub>5</sub> CN, C <sub>6</sub> H <sub>6</sub> , room temperature, 3 hr, then hydrolysis	C <sub>6</sub> H <sub>5</sub> COCH(C <sub>6</sub> H <sub>5</sub> )N(CH <sub>3</sub> ) <sub>2</sub> (72)	544
		C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH[C(OH)(C <sub>6</sub> H <sub>5</sub> )]N(CH <sub>3</sub> ) <sub>2</sub> (63)	544
		C <sub>6</sub> H <sub>5</sub> Na, C <sub>6</sub> H <sub>6</sub> , <i>n</i> -C <sub>8</sub> H <sub>18</sub> , reflux, 2 hr, then 20°, LiBr, ether, room temperature, 2.5 hr	 Room temperature, 4 hr, then overnight CH <sub>3</sub> COCH <sub>3</sub>	 (60) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> (27) C <sub>6</sub> H <sub>5</sub> CH[C(OH)(CH <sub>3</sub> ) <sub>2</sub> ]N(CH <sub>3</sub> ) <sub>2</sub> (41) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> (33)	544 544

TABLE II. AMINES (Continued)


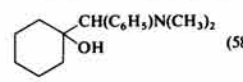
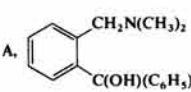
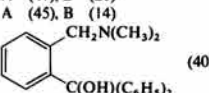
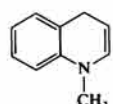
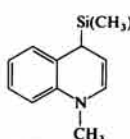
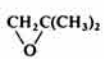
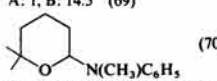
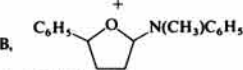
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>9</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Li, C <sub>6</sub> H <sub>6</sub> , n-C <sub>8</sub> H <sub>18</sub> , reflux 2 hr		 (58)	18, 544	
		C <sub>6</sub> H <sub>5</sub> K, room temperature, 18 hr	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH[C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ]N(CH <sub>3</sub> ) <sub>2</sub> (-)	18	
		n-C <sub>4</sub> H <sub>9</sub> Na, n-C <sub>6</sub> H <sub>14</sub>	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	A,  + B, C <sub>6</sub> H <sub>5</sub> CH[C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ]N(CH <sub>3</sub> ) <sub>2</sub>	18 18 18	
		15 min 2 hr 20 hr		A: 1, B: 1 (46) A: 1.7, B: 1 (75) A: 1, B: 0 (87)	18 18 18	
		n-C <sub>4</sub> H <sub>9</sub> Na, n-C <sub>6</sub> H <sub>14</sub> , then LiBr, 25-30°, ether		A, C <sub>6</sub> H <sub>5</sub> CH[C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ]N(CH <sub>3</sub> ) <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	18	
		1 hr 2 hr		A (47), B (21) A (45), B (14)	18	
		n-C <sub>4</sub> H <sub>9</sub> Na, n-C <sub>6</sub> H <sub>14</sub> , then LiBr, ether, 48°, 45 hr		 (40) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> (35) C <sub>2</sub> H <sub>5</sub> (CH <sub>3</sub> )C=C(CN)N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (-)	411	
		(CH <sub>3</sub> ) <sub>2</sub> C=C(CN)N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	n-C <sub>4</sub> H <sub>9</sub> Li, low temperature	CH <sub>3</sub> I	(i-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NC≡CCH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub> (80)	20
		(i-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NC≡CCH <sub>3</sub>	n-C <sub>4</sub> H <sub>9</sub> Li, ether, TMEDA, 0°, 8.5 hr	(CH <sub>3</sub> ) <sub>3</sub> SiCl, 0°	(i-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NC≡CCH <sub>2</sub> CH=CH <sub>2</sub> (40) + (i-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NC≡CCH <sub>3</sub> (14)	20
		n-C <sub>4</sub> H <sub>9</sub> Li, THF, -20°, 17 hr	CH <sub>2</sub> =CHCH <sub>2</sub> Br, 0°, 1.25 hr			20
C <sub>10</sub>	 C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH=CHCH <sub>3</sub> <i>cis</i>	(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> K, THF, -80°	(CH <sub>3</sub> ) <sub>3</sub> SiCl	 (25)	132a	
		t-C <sub>4</sub> H <sub>9</sub> OK: n-C <sub>4</sub> H <sub>9</sub> Li, 1: 1, petroleum ether, 0°, 30 min, then room temperature, 30 min	(CH <sub>3</sub> ) <sub>3</sub> SiCl	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH=CHCH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub> <i>cis</i> (71)	103	
		CH <sub>2</sub> =CHCH <sub>2</sub> N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	t-C <sub>4</sub> H <sub>9</sub> OK-n-C <sub>4</sub> H <sub>9</sub> Li, 1: 1, petroleum ether, 0°, 30 min, then room temperature, 30 min	CH <sub>3</sub> I	A, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH(CH <sub>3</sub> )CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH=CHC <sub>2</sub> H <sub>5</sub> <i>cis</i>	103
				A: 1, B: 16 (75)	103	
			n-C <sub>4</sub> H <sub>9</sub> Br	A, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH(C <sub>4</sub> H <sub>9</sub> -n)CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH=CHC <sub>5</sub> H <sub>11</sub> -n <i>cis</i>	103	
				A: 1, B: 14.5 (69)	103	
					 (70)	103
			C <sub>6</sub> H <sub>5</sub> CHO		A, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH(CHOHC <sub>6</sub> H <sub>5</sub> )CH=CH <sub>2</sub> + B, 	103
				(CH <sub>3</sub> ) <sub>3</sub> SiCl	A: 1, B: 1.11 (60) C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH=CHCH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub> (71) <i>cis</i>	103
			H <sub>2</sub> O		A, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH <sub>2</sub> CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH=CHCH <sub>3</sub> <i>cis</i>	103
	D <sub>2</sub> O		A: 1, B: 14 (81) A, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCHDCH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH=CHCH <sub>2</sub> D <i>cis</i>	103		
			A: 1, B: 13.8 (80)	103		

TABLE II. AMINES (Continued)

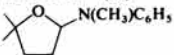


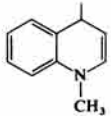
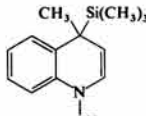
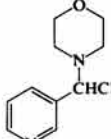
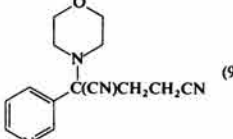



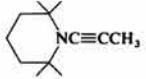
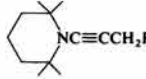
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>10</sub> (Contd.)	CH <sub>2</sub> =CHCH <sub>2</sub> N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	D <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CHO, (CH <sub>3</sub> ) <sub>3</sub> SiCl	A, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH[CH(OSi(CH <sub>3</sub> ) <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> ]CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH=CHCH <sub>2</sub> CH[OSi(CH <sub>3</sub> ) <sub>3</sub> ]C <sub>6</sub> H <sub>5</sub> <i>cis</i> A: 1, B: 1.22 (66)	103
			CH <sub>3</sub> COCH <sub>3</sub>	 (8) + A, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH <sub>2</sub> CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NCH=CHCH <sub>3</sub> <i>cis</i> A: 1, B: 6 (73) n-C <sub>2</sub> H <sub>11</sub> C≡CCH[CH(OH)C <sub>6</sub> H <sub>5</sub> ]N(CH <sub>3</sub> ) <sub>2</sub> (40)	103
	n-C <sub>2</sub> H <sub>11</sub> C≡CCH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	n-C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 1 hr ZnI <sub>2</sub> , THF, -70°, 1 hr	C <sub>6</sub> H <sub>5</sub> CHO	n-C <sub>2</sub> H <sub>11</sub> C≡CCH[CH(OH)C <sub>6</sub> H <sub>5</sub> ]N(CH <sub>3</sub> ) <sub>2</sub> (40)	30
	(CH <sub>3</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> N 	n-C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 1 hr, ZnI <sub>2</sub> , THF, -70°, 1 hr	C <sub>6</sub> H <sub>5</sub> CHO	(CH <sub>3</sub> ) <sub>3</sub> SiC≡CCH[CH(OH)C <sub>6</sub> H <sub>5</sub> ]N  (30)	30
C <sub>11</sub>	CH <sub>3</sub> CH=C(CN)N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	LDA, THF, -78°, 3 hr	CH <sub>3</sub> I	RCH <sub>2</sub> CH=C(CN)N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> A, R = CH <sub>3</sub> (76) A, R = C <sub>6</sub> H <sub>5</sub> CH(OH) (81) A, R = (CH <sub>3</sub> ) <sub>2</sub> C(OH) (63) A, R = (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C[OSi(CH <sub>3</sub> ) <sub>3</sub> ]	268 268 268 268
			C <sub>6</sub> H <sub>5</sub> CHO, then H <sub>2</sub> O CH <sub>3</sub> COCH <sub>3</sub> , then H <sub>2</sub> O C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> , then (CH <sub>3</sub> ) <sub>3</sub> SiCl		
		(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> K, THF, -80°	(CH <sub>3</sub> ) <sub>3</sub> SiCl	 (47)	132a
		KOH, t-C <sub>4</sub> H <sub>9</sub> OH	CH <sub>2</sub> =CHCN	 (90)	489
C <sub>12</sub>	C <sub>6</sub> H <sub>5</sub> CH=CHCH(CN)N(CH <sub>3</sub> ) <sub>2</sub>	LDA, THF, -78°, 3 hr	CH <sub>3</sub> I	A, C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )CH=C(CN)N(CH <sub>3</sub> ) <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> CH=CHC(CH <sub>3</sub> )(CN)N(CH <sub>3</sub> ) <sub>2</sub> A: 50, B: 50 (93)	268
			i-C <sub>3</sub> H <sub>7</sub> I	A, C <sub>6</sub> H <sub>5</sub> CH(C <sub>3</sub> H <sub>7</sub> -i)CH=C(CN)N(CH <sub>3</sub> ) <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> CH=CHC(C <sub>3</sub> H <sub>7</sub> -i)(CN)N(CH <sub>3</sub> ) <sub>2</sub> A: 73, B: 27 (75)	268
71		NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, room temperature	D <sub>2</sub> O, CO <sub>2</sub>	 (92)	343
			O <sub>2</sub>	 (NCOC <sub>6</sub> H <sub>5</sub> ) (-)	343
	CH <sub>3</sub> CH=C(CO <sub>2</sub> CH <sub>3</sub> )N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	LDA, THF, -12°, 2.5 hr LDA, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -12°	CH <sub>3</sub> I	C <sub>2</sub> H <sub>5</sub> CH=C(CO <sub>2</sub> CH <sub>3</sub> )N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (80)	268 268
		i-C <sub>4</sub> H <sub>9</sub> Li, TMEDA, ether, -78°, then 0°, then -50°, then 0°, 30 min	CH <sub>2</sub> =CHCH <sub>2</sub> I, 0°, overnight		20
			(CH <sub>3</sub> ) <sub>3</sub> SiCl, 0°, overnight	A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (45)	20
			CH <sub>3</sub> I, 0°, overnight	A, R = (CH <sub>3</sub> ) <sub>3</sub> Si (60)	20
			n-C <sub>4</sub> H <sub>9</sub> I, 0°, overnight	A, R = CH <sub>3</sub> (35)	20
				A, R = C <sub>4</sub> H <sub>9</sub> -n (50)	20

TABLE II. AMINES (Continued)

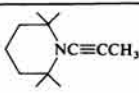
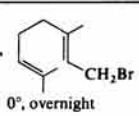
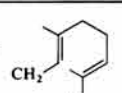
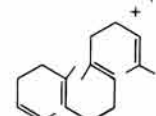

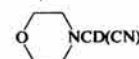
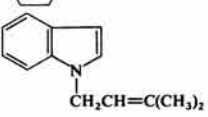
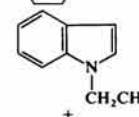
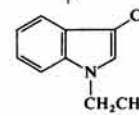
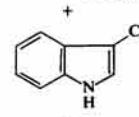
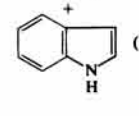

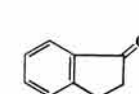
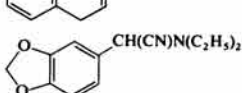
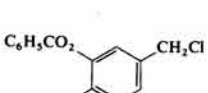
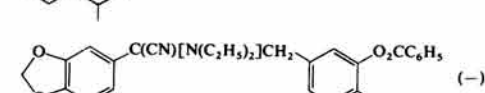

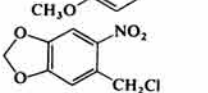
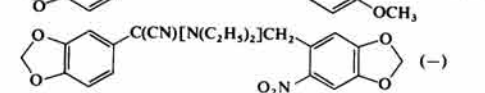

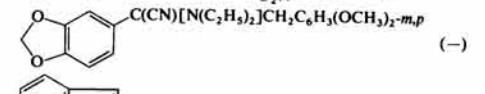
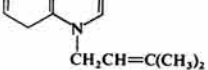
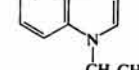
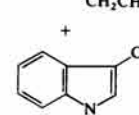
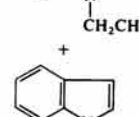
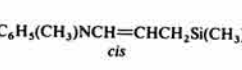
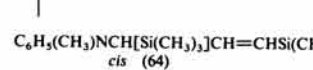
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>12</sub> (Contd.)		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, ether, -78°, then 0°, then -50°, then 0°, 30 min	 0°, overnight	A, R =  (40) +  cis and trans (11)	20
C <sub>13</sub> 72		NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, room temperature	D <sub>2</sub> O, CO <sub>2</sub>	 (95)	343
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA,	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Cl	 (40) +  (30) +  (5) +  (10)	100
73		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>14</sub> , -65°	CH <sub>3</sub> I, H <sub>2</sub> O	 (85)	19
		NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, room temperature, 1 hr		 (-)	330
				 (-)	330
			<i>m,p</i> -(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> Cl	 (-)	330
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Cl, then aromatization	 (60) +  (20) +  (10)	100
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, petroleum ether, 0°, 30 min, then room temperature, 30 min	(CH <sub>3</sub> ) <sub>3</sub> SiCl	 (64)	103

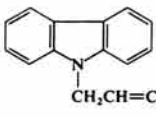
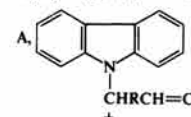
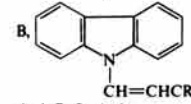
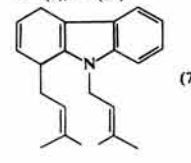
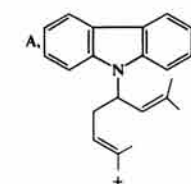
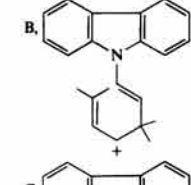
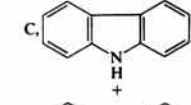
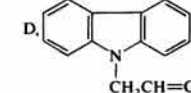
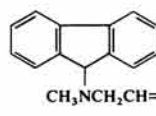
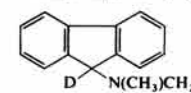
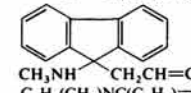
TABLE II. AMINES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>14</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , -65°	CH <sub>3</sub> I, H <sub>2</sub> O	(95)	19
74		NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, room temperature	D <sub>2</sub> O, CO <sub>2</sub>	(99)	343
		NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, room temperature	D <sub>2</sub> O, CO <sub>2</sub>	(94)	343
	<i>m,p</i> -(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH(CN)N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, room temperature, 1 hr	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	<i>m,p</i> -(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> C(CN)[N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ]R A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-)	330
			<i>m,p</i> -(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> Cl	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (OCH <sub>3</sub> )- <i>m,p</i> (-)	330
			<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl- <i>o</i> (-)	330
			<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (-)	330
			<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i> (-)	330
		<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> (-)	330	
		<i>o</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>o</i> (-)	330	
C <sub>15</sub>		KNH <sub>2</sub> , NH <sub>3</sub> (liq), reflux, 1 hr	H <sub>2</sub> O	(60)	187
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, reflux, 13 hr		(56)	187
75		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.1 eq), TMEDA (1.1 eq), ether, -15°, 1.5 hr	RX	A, B,	102
			RX = D <sub>2</sub> O	A: 25, B: 75; <i>cis</i> : 85, <i>trans</i> : 15 (-)	102
			RX = <i>i</i> -C <sub>3</sub> H <sub>7</sub> Cl	A (3), B (80)	102
			RX = <i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl	A (6), B (80)	102
			RX = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	A (5), B (75)	102
			RX = CH <sub>3</sub> COCH <sub>3</sub>	A (23), B (38)	102
			RX = (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CO	A (25), B (60)	102
75		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA or DABCO	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Cl		100
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Cl	A, R = CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (80) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (30) + A, R = CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (60) + A, R = C[CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (10)	100
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Cl, then aromatization	A, R = C[CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (10) + A, R = CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (-)	100
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, 25°, 48 hr	D <sub>2</sub> O	1.02 D	448
	C <sub>6</sub> H <sub>5</sub> CH=CHCH(CN)N	LDA, THF, -78°, 3 hr	CH <sub>3</sub> I	A, C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )CH=C(CN)N + B, C <sub>6</sub> H <sub>5</sub> CH=CHC(CH <sub>3</sub> )(CN)N A: 44, B: 56 (87)	268

TABLE II. AMINES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>15</sub> (Contd.)		LDA, THF, -78°, 3 hr	<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	A. C <sub>6</sub> H <sub>5</sub> CH(C <sub>3</sub> H <sub>7</sub> - <i>η</i> )CH=C(CN)N-cyclohexyl + B. C <sub>6</sub> H <sub>5</sub> CH=CHC(C <sub>3</sub> H <sub>7</sub> - <i>η</i> )(CN)N-cyclohexyl	268
C <sub>16</sub> 76		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.1 eq), TMEDA (1.1 eq), ether, -15°, 1 hr	RX	A. B.	A: 63, B: 37 (70)
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.1 eq), TMEDA (1.1 eq), ether, -15°, 2.5 hr	RX	A. B.	A: 15, B: 85 (-) A (0), B (72) A (0), B (85) A (0), B (45) A (0), B (75)
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.1 eq), TMEDA (1.1 eq), ether, -15°, 4 hr	RX	A. B.	RX = D <sub>2</sub> O RX = <i>i</i> -C <sub>3</sub> H <sub>7</sub> Cl RX = <i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl RX = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl RX = (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CO A: 40, B: 60 (-) A (0), B (70) A (0), B (70) A (0), B (70) A (10), B (70)
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.1 eq), TMEDA (1.1 eq), ether, -15°, 4 hr	RX	A. B.	RX = D <sub>2</sub> O RX = <i>i</i> -C <sub>3</sub> H <sub>7</sub> Cl RX = <i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl A: 8, B: 2 (-) A (0), B (26) A (14), B (20)
C <sub>15</sub> 77		NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, 40°	D <sub>2</sub> O, CO <sub>2</sub>		(97)
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 0°, 2 hr	CH <sub>3</sub> I, 0°, 5 min		C <sub>6</sub> H <sub>5</sub> CHRCH=CHN(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> <i>cis</i> A, R = CH <sub>3</sub> (76) A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (62.6) A, R = CH <sub>2</sub> C[OSi(CH <sub>3</sub> ) <sub>3</sub> ](CH <sub>3</sub> ) <sub>2</sub> (84)
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 0°, 2 hr	(CH <sub>3</sub> ) <sub>3</sub> SiCl CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> , 	A, R = CH[OSi(CH <sub>3</sub> ) <sub>3</sub> ]C <sub>6</sub> H <sub>5</sub> (90)	264
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 0°, 2 hr	C <sub>6</sub> H <sub>5</sub> CHO, -78°, then (CH <sub>3</sub> ) <sub>3</sub> SiCl D <sub>2</sub> O	A. C <sub>6</sub> H <sub>5</sub> CHDCH=CHN(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> <i>cis</i> + B. C <sub>6</sub> H <sub>5</sub> CH=CHCHDN(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> <i>trans</i>	264
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 0°	D <sub>2</sub> O, 0°, 1 hr	A: 2, B: 1 A, C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NC(C <sub>6</sub> H <sub>5</sub> )=CHCH <sub>2</sub> R A, R = D (87)	113

TABLE II. AMINES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>16</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NC(C <sub>6</sub> H <sub>5</sub> )=CHCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 0°	CH <sub>3</sub> I, 0°, 1 hr C <sub>6</sub> H <sub>5</sub> CHO, -78°, 1 hr CH <sub>3</sub> COCH <sub>3</sub> , -78°, 1 hr (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> , 0°, 1 hr	A, R = CH <sub>3</sub> (85) A, R = CH(OH)C <sub>2</sub> H <sub>5</sub> (-) A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (-) A, R = CH <sub>2</sub> C(OH)(CH <sub>3</sub> ) <sub>2</sub> (85)	113 113 113 113	
C <sub>17</sub>	C <sub>6</sub> H <sub>5</sub> CH=CHCH(CN)N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> 	LDA, THF, -78°, 2 hr  <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.1 eq), TMEDA (1.1 eq), ether, -15°, 15 hr	CH <sub>3</sub> I <i>i</i> -C <sub>3</sub> H <sub>7</sub> Br  RX	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )CH=C(CN)N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (74) C <sub>6</sub> H <sub>5</sub> CH(C <sub>2</sub> H <sub>5</sub> - <i>η</i> )CH=C(CN)N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (-)  A,  + B, 	268 268	
			RX = D <sub>2</sub> O RX = <i>i</i> -C <sub>3</sub> H <sub>7</sub> Cl RX = <i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl (CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Cl	A: 1, B: 0 (-) A (0), B (6) A (12), B (15) A (3), B (23)	102	
		Na, NH <sub>3</sub> (liq)	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Cl	 (70)	101	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA or DABCO	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Cl	A,  + B,  + C,  + D, 	A (3), B (20), C (15), D (-) A: 10, B: 40, C: 50 (-)	101 101
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (0.5 eq), DABCO  <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, room temperature, 1 day	- D <sub>2</sub> O	 (-)	195	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, reflux, 7 hr	H <sub>2</sub> O	 (44)	195	
	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NC(C <sub>6</sub> H <sub>5</sub> )=C(CH <sub>3</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 0°, 24 hr	CH <sub>3</sub> I	CH <sub>3</sub> NH-CH <sub>2</sub> CH=CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NC(C <sub>6</sub> H <sub>5</sub> )=C(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> ) (70)	113	
	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NC(C <sub>6</sub> H <sub>5</sub> )=CHC <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 0°, 30 hr	CH <sub>3</sub> I, 0°, 1 hr	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NC(C <sub>6</sub> H <sub>5</sub> )=CHC <sub>2</sub> H <sub>5</sub> - <i>i</i> (85)	113	

78

79



TABLE II. AMINES (Continued)






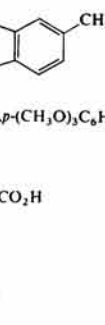

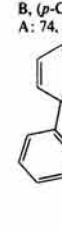
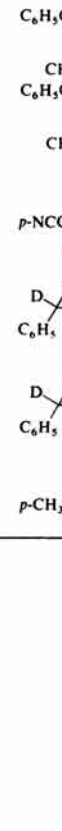


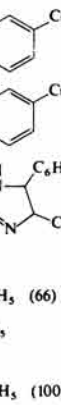




No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>17</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CH=CHCH(CN)N(CH <sub>3</sub> )C <sub>6</sub> H <sub>11</sub>	LDA, THF, -78°, 3 hr	CH <sub>3</sub> I i-C <sub>3</sub> H <sub>7</sub> I	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )CH=C(CN)N(CH <sub>3</sub> )C <sub>6</sub> H <sub>11</sub> (71) C <sub>6</sub> H <sub>5</sub> CH(C <sub>3</sub> H <sub>7</sub> -i)CH=C(CN)N(CH <sub>3</sub> )C <sub>6</sub> H <sub>11</sub> (64)	268 268
C <sub>18</sub>	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NC(C <sub>6</sub> H <sub>5</sub> )=CHC <sub>3</sub> H <sub>7</sub> -i	n-C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 0°	CH <sub>3</sub> I, 0°, 1 hr	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )NC(C <sub>6</sub> H <sub>5</sub> )=CHC <sub>4</sub> H <sub>9</sub> -i (80)	113
C <sub>19</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	n-C <sub>4</sub> H <sub>9</sub> Li, THF, 25°, 1 hr	D <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NCHDC <sub>6</sub> H <sub>5</sub> (90)	194
C <sub>20</sub>	 NCH(CN)C <sub>6</sub> H <sub>5</sub> (OCH <sub>3</sub> -m)(OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> -p)	NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, room temperature	D <sub>2</sub> O, CO <sub>2</sub>	 NCD(CN)C <sub>6</sub> H <sub>5</sub> (OCH <sub>3</sub> -m)(OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> -p) (100)	343
C <sub>21</sub>	(C <sub>6</sub> H <sub>5</sub> CH=N) <sub>2</sub> CHC <sub>6</sub> H <sub>5</sub>	KNH <sub>2</sub> , NH <sub>3</sub> (liq), reflux, 1 hr	H <sub>2</sub> O	 (63)	187
		C <sub>6</sub> H <sub>5</sub> Li, THF, -78° to 25°, 270 min	CH <sub>3</sub> CO <sub>2</sub> H	<i>cis</i> (88)	187,188
	( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH=N) <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	C <sub>6</sub> H <sub>5</sub> Li, THF, -78°, 30 min	CH <sub>3</sub> CO <sub>2</sub> H	A,  B, ( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH=N) <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> A: 74, B: 26 (78)	187,188
	 NCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	n-C <sub>4</sub> H <sub>9</sub> Li, THF, 25°, 72 hr	D <sub>2</sub> O	 NCHDC <sub>6</sub> H <sub>5</sub> (-)	194
	 CH(CN)N(CH <sub>3</sub> )CH <sub>2</sub> CH(OCH <sub>3</sub> ) <sub>2</sub>	NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, room temperature, 1 hr	 CH <sub>2</sub> Cl	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> -  C(CN)[N(CH <sub>3</sub> )CH <sub>2</sub> CH(OCH <sub>3</sub> ) <sub>2</sub> ]CH <sub>2</sub> -  CH <sub>2</sub> (-) 330	
			<i>m,m'</i> -p-(CH <sub>3</sub> O) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CH <sub>2</sub> Cl	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> -  C(CN)[N(CH <sub>3</sub> )CH <sub>2</sub> CH(OCH <sub>3</sub> ) <sub>2</sub> ]CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (OCH <sub>3</sub> ) <sub>3</sub> - <i>m,m',p</i> (-)	330
C <sub>24</sub>	( <i>p</i> -NCC <sub>6</sub> H <sub>4</sub> CH=N) <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub> CN- <i>p</i>	C <sub>6</sub> H <sub>5</sub> Li, THF, -78°, 1 min	CH <sub>3</sub> CO <sub>2</sub> H	 (100)	188
C <sub>26</sub>		NaH, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -10°, 3 days	D <sub>2</sub> O	 (66)	558
		NaH, CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , -78°, 5 days	D <sub>2</sub> O	 (100)	558
	( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH=N) <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	C <sub>6</sub> H <sub>5</sub> Li, THF, -78° to 25°, 1000 min	CH <sub>3</sub> CO <sub>2</sub> H	 (42)	187,188

TABLE III. BORANES<sup>a</sup>

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>15</sub>	$[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BCH}=\text{CHC}_3\text{H}_7-n$	LTMP, THF, 25°, 15 min	(CH <sub>3</sub> ) <sub>3</sub> SiCl	$[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BCH}=\text{CHCH}[\text{Si}(\text{CH}_3)_3]\text{C}_2\text{H}_5$ (not isolated)	17
C <sub>16</sub>	$[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BCH}=\text{CHC}_4\text{H}_9-n$	LTMP, THF, 25°, 15 min	(CH <sub>3</sub> ) <sub>3</sub> SiCl	$[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BCH}=\text{CHCH}[\text{Si}(\text{CH}_3)_3]\text{C}_3\text{H}_7-n$ (not isolated)	17
	$[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BC}(\text{C}_2\text{H}_5)=\text{CHC}_2\text{H}_5$			$[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BC}(\text{C}_2\text{H}_5)=\text{CHCH}[\text{Si}(\text{CH}_3)_3]\text{CH}_3$ (not isolated)	17
8 C <sub>18</sub>	$[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BCH}=\text{CHC}_6\text{H}_{13}-n$	LTMP, THF, 25°, 15 min	CH <sub>3</sub> I, 25°, 15 min	$[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BCH}(\text{CH}_3)\text{CH}=\text{CHC}_5\text{H}_{11}-n$ + $[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BC}(\text{CH}_3)=\text{CHC}_6\text{H}_{13}-n$ A: 81, B: 19 (not isolated)	17
			(CH <sub>3</sub> ) <sub>3</sub> SiCl	$[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BCH}=\text{CHCH}[\text{Si}(\text{CH}_3)_3]\text{C}_5\text{H}_{11}-n$ (not isolated)	17
			H <sub>2</sub> O	A, $[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BCH}_2\text{CH}=\text{CHC}_5\text{H}_{11}-n$ + B, $[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BCH}=\text{CHC}_6\text{H}_{13}-n$ A: 82, B: 18 (not isolated)	17
			CH <sub>3</sub> COCH <sub>3</sub> , 25°, 15 min	$[(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)]_2\text{BCH}=\text{CHCH}[\text{COH}(\text{CH}_3)_2]\text{C}_5\text{H}_{11}-n$ (not isolated)	17

<sup>a</sup> The reaction of a diisoamylborane with an acetylenic compound gives the vinylborane, which is metalated *in situ*.

TABLE IV. BROMIDES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>3</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> Br	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiLi (1 eq), ether, room temperature, 4 hr	H <sub>3</sub> O <sup>+</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH <sub>2</sub> CH=CH <sub>2</sub> (11) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>3</sub> (7.1) +	413
		LDA (0.5 eq), THF, -78°, 1 hr, then 0°, 1 hr	HCl, <i>N</i>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=CHCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (1.8) CH <sub>2</sub> =CHCHBrCH <sub>2</sub> CH=CH <sub>2</sub> (44)	615
C <sub>5</sub>	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Br	LDA (0.5 eq), THF, -78°, 1 hr, then 0°, 1 hr	HCl, <i>N</i>	A, (CH <sub>3</sub> ) <sub>2</sub> C=CHCH=CHCH=C(CH <sub>3</sub> ) <sub>2</sub> <i>cis</i> and <i>trans</i> + B, CH <sub>2</sub> =C(CH <sub>3</sub> )CH=CHCH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> A (18), B (18)	615
C <sub>7</sub>	C <sub>6</sub> H <sub>5</sub> CHBr <sub>2</sub>	LDA, THF-ether, 7:10, -110°, 15 min	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO-THF (3:5)	C <sub>6</sub> H <sub>5</sub> CBr=CHC <sub>3</sub> H <sub>7-n</sub> (-)	595
			<i>i</i> -C <sub>3</sub> H <sub>7</sub> CHO, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO-THF (3:5) -110° to 15°, 2 hr	C <sub>6</sub> H <sub>5</sub> COCHBrC <sub>3</sub> H <sub>7-i</sub> (57)	595

TABLE IV. BROMIDES (Continued)


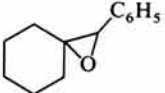
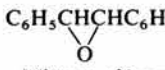
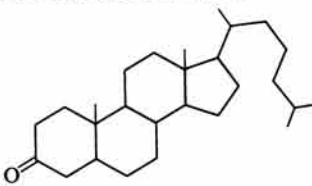
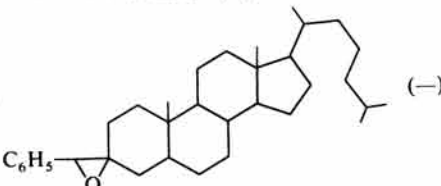
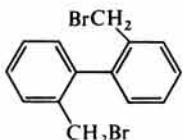


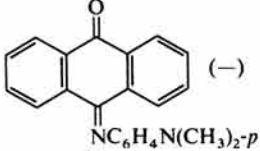
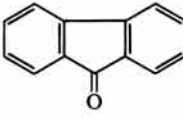
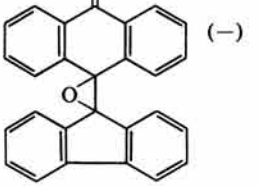
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>7</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CHBr <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), THF, -78°		 (-)	359
			-78°, 1 hr, then room temperature, 6 hr	C <sub>6</sub> H <sub>5</sub> CHCHC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (-),  (-)	359 359
			<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHO, -78°, 1 hr, then room temperature, 6 hr	Mixture of isomers (-)	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	—	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (0.5 eq), THF, -100°, 2 hr		 (-)	359
			-78°, 1 hr, then room temperature, 6 hr	Mixture of isomers	
			—	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (88) + C <sub>6</sub> H <sub>5</sub> C <sub>5</sub> H <sub>11-n</sub> (12)	60,111
		LDA (0.6 eq), THF, -78°, 1 hr, then 0°, 1 hr	HCl, <i>N</i>	C <sub>6</sub> H <sub>5</sub> CHBrCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (100)	615
C <sub>10</sub>	C <sub>2</sub> H <sub>5</sub> CH(Br)C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i>	NaNH <sub>2</sub> (excess), NH <sub>3</sub> (liq)	—	( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> )(C <sub>2</sub> H <sub>5</sub> )C=C(C <sub>2</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> ) (-)	458
C <sub>14</sub>		NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	—	 (80)	459
			K <sub>2</sub> CO <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> OH, reflux, 10 hr	(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> NO- <i>p</i>	 (-)
		K <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH, reflux, 2 hr		 (-)	344

TABLE V. CHLORIDES

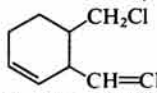
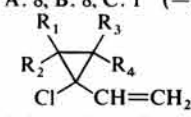
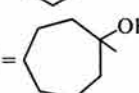
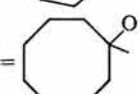
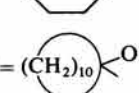
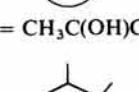

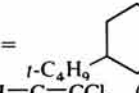
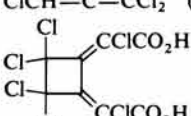
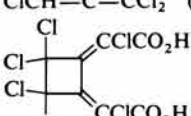
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>3</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> Cl	NaNH <sub>2</sub> , NH <sub>3</sub> (liq), inverse addition	—	CH <sub>2</sub> =CHCH=CHCH=CH <sub>2</sub> (30) +  (-)	57	
		LDA (0.5 eq), THF, -78°, 1 hr, then 0°, 1 hr	HCl, N	A, CH <sub>2</sub> =CHCH(Cl)CH <sub>2</sub> CH=CH <sub>2</sub> + B, CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>2</sub> CH=CHCl A: 8, B: 1 (23)	615	
		LDA (1 eq), THF, -78°	CH <sub>2</sub> =CHCH <sub>2</sub> Br (1 eq), -78°, 1 hr, then room temperature	A, CH <sub>2</sub> =CHCHBrCH <sub>2</sub> CH=CH <sub>2</sub> + B, CH <sub>2</sub> =CHCHClCH <sub>2</sub> CH=CH <sub>2</sub> + C, CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>2</sub> CH=CHCl A: 8, B: 8, C: 1 (-)	615	
	CH <sub>2</sub> =CHCHCl <sub>2</sub>	LTMP, ether, -5°, 1 hr, in presence of olefin	(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub>		A, R <sub>1</sub> = R <sub>2</sub> = R <sub>3</sub> = R <sub>4</sub> = CH <sub>3</sub> (28)	135d
					A, R <sub>1</sub> = R <sub>2</sub> = R <sub>3</sub> = CH <sub>3</sub> , R <sub>4</sub> = H (25)	135d
					A, R <sub>1</sub> = R <sub>2</sub> = CH <sub>3</sub> , R <sub>3</sub> = R <sub>4</sub> = H (42)	135d
					A, R <sub>1</sub> = R <sub>3</sub> = CH <sub>3</sub> , R <sub>2</sub> = R <sub>4</sub> = H (39)	135d
					A, R <sub>1</sub> = R <sub>4</sub> = CH <sub>3</sub> , R <sub>2</sub> = R <sub>3</sub> = H (30)	135d
					A, R <sub>1</sub> = CH=CH <sub>2</sub> , R <sub>2</sub> = R <sub>3</sub> = R <sub>4</sub> = H (not isolated)	135d
					CH <sub>2</sub> =CHCHCl <sub>2</sub>	LDA, THF, -78°, 2 hr
A, R =  (63)	616					
A, R =  (68)	616					
A, R =  (66)	616					
A, R = CH <sub>3</sub> C(OH)C <sub>6</sub> H <sub>13-n</sub> (73)	616					
A, R =  (50)	616					
A, R =  (54)	616					
A, R =  (76)	553					
A, R =  (90)	168					
C <sub>3</sub>	ClCH=CClCHCl <sub>2</sub>	NaNH <sub>2</sub> , -75°, 15 hr	—	ClCH=C=CCl <sub>2</sub> (76)		
		n-C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF-ether-petroleum ether, 4:1:1, -110°	CO <sub>2</sub> , -90° to 20°, then H <sup>+</sup>	 (90)	168	

TABLE V. CHLORIDES (Continued)


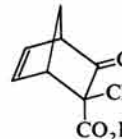
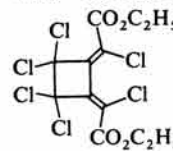

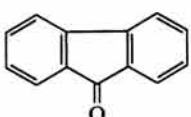
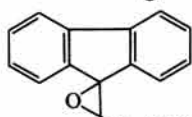
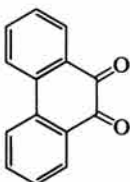
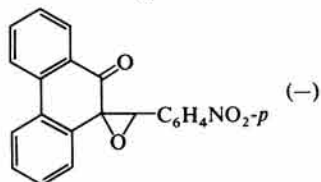
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>3</sub> (Contd.)	ClCH=CClCHCl <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF-ether-petroleum ether, 4:1:1, -110°	CO <sub>2</sub> , then 	 (91)	168
C <sub>4</sub>	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> Cl	NaNH <sub>2</sub> (1 eq), NH <sub>3</sub> (liq) NaNH <sub>2</sub> (0.5 eq), NH <sub>3</sub> (liq)	— —	CH <sub>2</sub> =C(CH <sub>3</sub> )CH=CHC(CH <sub>3</sub> )=CH <sub>2</sub> (27) CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> CHClC(CH <sub>3</sub> )=CH <sub>2</sub> (-) + CH <sub>2</sub> =C(CH <sub>3</sub> )CH=CHC(CH <sub>3</sub> )=CH <sub>2</sub> (-)	457 457
88 C <sub>6</sub>	Cl <sub>2</sub> C=CClCHClCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OLi, C <sub>3</sub> H <sub>8</sub> , -75°, 9 hr	—	 (86)	554
C <sub>7</sub>	C <sub>6</sub> H <sub>5</sub> CCl <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -100°, 1.25 hr	CO <sub>2</sub> , then H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> COCO <sub>2</sub> H (75)	160
			CH <sub>3</sub> I, 3 hr H <sub>2</sub> O CH <sub>3</sub> OD	C <sub>6</sub> H <sub>5</sub> CCl <sub>2</sub> CH <sub>3</sub> (77) C <sub>6</sub> H <sub>5</sub> CHCl <sub>2</sub> (58) C <sub>6</sub> H <sub>5</sub> CDCl <sub>2</sub> (-)	160 160 160
		-105°, 45 min	(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub> , -105°, then -65°	 (72)	160
	<i>o,p</i> -Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> Cl	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (0.5 eq), THF, -100°, 2 hr	—	<i>o,p</i> -Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> CHClC <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> - <i>o,p</i> (50) + <i>o,p</i> -Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH=CHC <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> - <i>o,p</i> (-) + <i>o,p</i> -Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> Cl (-)	111
	<i>o</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	K <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH, reflux, 4 hr Reflux, 2 hr	(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> NO- <i>p</i> <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	<i>o</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=NC <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> - <i>p</i> (-) <i>o</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHCHC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i> (-)	344 344
		Reflux, 2 hr		 (-)	344
	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	K <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH, reflux, 2.5 hr	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> CHCHC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i> (-)	344
			<i>o</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHCHC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>o</i> (-)	344
			<i>m</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHCHC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>m</i> (-)	344
			<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHCHC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i> (-)	344
			<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHCHC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> (-)	344
			(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCHO	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHCHCH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (-)	344
		Reflux, 2 hr	C <sub>6</sub> H <sub>5</sub> COCOC <sub>6</sub> H <sub>5</sub> (0.5 eq)	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHC(C <sub>6</sub> H <sub>5</sub> )COC <sub>6</sub> H <sub>5</sub> (-)	344
				 (-)	344

TABLE V. CHLORIDES (Continued)

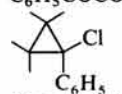
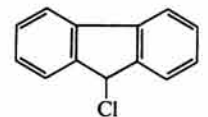
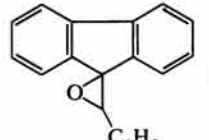
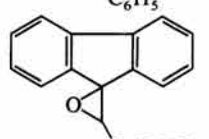
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>7</sub> (Contd.)	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	K <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH, reflux, 2.5 hr	(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> NO- <i>p</i>	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=NC <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> - <i>p</i> (-)	344
	C <sub>6</sub> H <sub>5</sub> CHCl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub> , C <sub>3</sub> H <sub>7</sub> OH, reflux, 6 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), THF-petroleum ether-ether, 96:24:24, -100°, 30 min <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -90°, 15 min	[ <i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ] <sub>2</sub> CS CO <sub>2</sub> , H <sub>2</sub> O	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=C[C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> - <i>p</i> ] <sub>2</sub> (-) C <sub>6</sub> H <sub>5</sub> COCO <sub>2</sub> H (61)	344 112
06	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (0.5 eq), THF, -100°, 1.5 hr	(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub> , -100°, 1 hr, then then -65° to -40°	C <sub>6</sub> H <sub>5</sub> COCO <sub>2</sub> H (42)	160
	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (0.5 eq), THF, -100°, 1.5 hr	(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub>	 (48)	160
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (0.5 eq), THF, -100°, 2 hr	—	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (33)	160
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (0.5 eq), THF, -100°, 15 min, then -100° to -80°, 2.5 hr	—	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CHClC <sub>6</sub> H <sub>4</sub> Cl- <i>o</i> (80)	111
		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NLi (0.5 eq), ether-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 1:1, -70°, 1 hr, inverse addition	—	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CHClC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (95)	111
		LDA (0.5 eq), THF, -78°, 1 hr, then 0°, 1 hr	HCl, <i>N</i>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHClC <sub>6</sub> H <sub>5</sub> (80)	60
		LiNH <sub>2</sub> or NaNH <sub>2</sub> (0.33 eq), ether, NH <sub>3</sub> (liq), -70°, 15 min, inverse addition,	—	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl (8)	111
			—	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHClC <sub>6</sub> H <sub>5</sub> (86) C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl (60)	550
			—	C <sub>6</sub> H <sub>5</sub> CHClCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (10) C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (25)	
			—	<i>trans</i> C <sub>6</sub> H <sub>5</sub> CHClCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (90)	615
		—	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHClC <sub>6</sub> H <sub>5</sub> (74-79)	426	
		NaNH <sub>2</sub> (0.5 eq), NH <sub>3</sub> (liq)	—	C <sub>6</sub> H <sub>5</sub> CHCHClC <sub>6</sub> H <sub>5</sub> (20-25)	426
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 45 min	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> Cl	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (40-45) C <sub>6</sub> H <sub>5</sub> CH=CHC(CH <sub>3</sub> )=CH <sub>2</sub> (23)	459
			CH <sub>2</sub> =CHCH <sub>2</sub> Cl	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (13) CH <sub>2</sub> =C(CH <sub>3</sub> )CH=CHC(CH <sub>3</sub> )=CH <sub>2</sub> (35)	
				polymers C <sub>6</sub> H <sub>5</sub> CH=CHCH=CH <sub>2</sub> (15)	459
				C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (-)	
				CH <sub>2</sub> =CHCH=CHCH=CH <sub>2</sub> (-)	
				C <sub>6</sub> H <sub>5</sub> CHCHC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i> (-)	444
16	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (0.5 eq), THF, -100°, 3 hr	—	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CHClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> (-)	111
	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (0.5 eq), THF, -100°, 3 hr	—	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CHClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (91)	111
	C <sub>6</sub> H <sub>5</sub> CHClCH <sub>3</sub>	NaNH <sub>2</sub> (1.3 eq), NH <sub>3</sub> (liq), 1.5 hr	—	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )C(CH <sub>3</sub> )ClC <sub>6</sub> H <sub>5</sub> (-)	458
C <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> Cl	NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 15 min	—	C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHCH=CHC <sub>6</sub> H <sub>5</sub> (10)	459
	C <sub>6</sub> H <sub>5</sub> CHClC <sub>2</sub> H <sub>5</sub>	NaNH <sub>2</sub> (3 eq), NH <sub>3</sub> (liq), C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	—	C <sub>6</sub> H <sub>5</sub> (C <sub>2</sub> H <sub>5</sub> )C=C(C <sub>2</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>5</sub> ) (-)	458
C <sub>13</sub>		KOH, CH <sub>3</sub> OH, reflux, 1 hr	C <sub>6</sub> H <sub>5</sub> CHO	 (-)	344
		K <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH, reflux, 12 hr	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	 (-)	344

TABLE V. CHLORIDES (Continued)

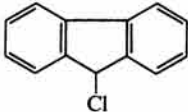
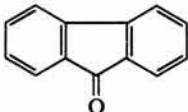
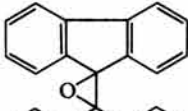

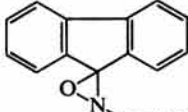
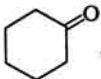
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.		
C <sub>13</sub> (Contd.)		Reflux, 4.5 hr		 (-)	344		
		K <sub>2</sub> CO <sub>3</sub> , C <sub>3</sub> H <sub>7</sub> OH, reflux, 6 hr	[ <i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ] <sub>2</sub> CS	 (-) C[C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> - <i>p</i> ] <sub>2</sub>	344		
		Reflux, 2 hr	(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> NO- <i>p</i>	 (-) C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> - <i>p</i>	344		
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CCl <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCl		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -100°, 1.25 hr	CO <sub>2</sub> , then H <sup>+</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH)CO <sub>2</sub> H (40)	160		
		NaNH <sub>2</sub> (0.5 eq), ether, NH <sub>3</sub> (liq), -70°, 15 min, inverse addition	—	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHC(Cl)(C <sub>6</sub> H <sub>5</sub> ) (60)	426		
		KNH <sub>2</sub> (0.5 eq), NH <sub>3</sub> (liq), inverse addition	CH <sub>3</sub> I	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CH <sub>2</sub> (40)	426		
		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NLi, ether-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 1:1, -75°	CH <sub>3</sub> I	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (80) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CH <sub>2</sub> (10)	550		
C <sub>14</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHClC <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), THF, -58° to -40°, 1.5 hr	—	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )C <sub>6</sub> H <sub>5</sub> (10) + C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (30) <i>trans</i>	111		
C <sub>21</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> PbCH <sub>2</sub> CH=CCl <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -90°, 20 min	C <sub>2</sub> H <sub>5</sub> CHO, -90°, 5 min	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (13) C <sub>2</sub> H <sub>5</sub> CH(OH)CCl <sub>2</sub> CH=CH <sub>2</sub> (69)	155		
			C <sub>6</sub> H <sub>5</sub> CHO, -90°, 5 min CH <sub>3</sub> COCH <sub>3</sub> , -90°, 5 min	C <sub>2</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> CH=CCl <sub>2</sub> (28) C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> CH=CCl <sub>2</sub> (97) (CH <sub>3</sub> ) <sub>2</sub> C(OH)CCl <sub>2</sub> CH=CH <sub>2</sub> (90)	155 155		
			-90°, 5 min CF <sub>3</sub> COCF <sub>3</sub> , -90°, 5 min CH <sub>3</sub> COC <sub>4</sub> H <sub>9</sub> - <i>t</i> , -90°, 5 min	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> , -90°, 5 min, then (CH <sub>3</sub> ) <sub>3</sub> SiCl	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> , -90°, 5 min, then (CH <sub>3</sub> ) <sub>3</sub> SiCl	(CF <sub>3</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> CH=CCl <sub>2</sub> (90)	155
						<i>t</i> -C <sub>4</sub> H <sub>9</sub> C(OH)(CH <sub>3</sub> )C(Cl)=CHCH <sub>2</sub> Cl (28) + <i>t</i> -C <sub>4</sub> H <sub>9</sub> C(OH)(CH <sub>3</sub> )C(Cl)=CHCH <sub>2</sub> OH (64)	155
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -95°, 1 hr	(CH <sub>3</sub> ) <sub>3</sub> SiCl (CH <sub>3</sub> ) <sub>3</sub> SnBr HgCl <sub>2</sub> (CH <sub>3</sub> ) <sub>3</sub> GeCl	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> , -90°, 5 min, then (CH <sub>3</sub> ) <sub>3</sub> SiCl	C <sub>6</sub> H <sub>5</sub> C[OSi(CH <sub>3</sub> ) <sub>3</sub> ](CH <sub>3</sub> )CCl <sub>2</sub> CH=CH <sub>2</sub> (29) + C <sub>6</sub> H <sub>5</sub> C[OSi(CH <sub>3</sub> ) <sub>3</sub> ](CH <sub>3</sub> )CH <sub>2</sub> CH=CCl <sub>2</sub> (18)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> CH=CCl <sub>2</sub> (91)	155
						(CH <sub>3</sub> ) <sub>3</sub> SiCl (CH <sub>3</sub> ) <sub>3</sub> SnBr HgCl <sub>2</sub> (CH <sub>3</sub> ) <sub>3</sub> GeCl	(CH <sub>3</sub> ) <sub>3</sub> SiCl <sub>2</sub> CH=CH <sub>2</sub> (99) (CH <sub>3</sub> ) <sub>3</sub> SnCH <sub>2</sub> CH=CCl <sub>2</sub> (97) ClHgCH <sub>2</sub> CH=CCl <sub>2</sub> (83) (CH <sub>3</sub> ) <sub>3</sub> GeCl <sub>2</sub> CH=CH <sub>2</sub>
			(CH <sub>3</sub> ) <sub>3</sub> GeCl (0.5 eq)		(CH <sub>3</sub> ) <sub>3</sub> GeCH <sub>2</sub> CH=CCl <sub>2</sub> A: 5.66, B: 1 (100) A, (CH <sub>3</sub> ) <sub>3</sub> GeCl <sub>2</sub> CH=CH <sub>2</sub> + B, (CH <sub>3</sub> ) <sub>3</sub> GeCH <sub>2</sub> CH=CCl <sub>2</sub> A: 0.65, B: 1 (-)	159	



TABLE VI. CYANOHYDRIN ETHERS



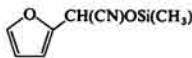






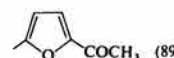





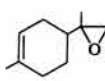
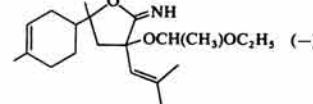
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>7</sub>	CH <sub>2</sub> =CHCH(CN)OSi(CH <sub>3</sub> ) <sub>3</sub>	LDA, THF, -78°, 2 hr	CH <sub>3</sub> I <i>i</i> -C <sub>3</sub> H <sub>7</sub> I	CH <sub>2</sub> =CHC(CH <sub>3</sub> )(CN)OSi(CH <sub>3</sub> ) <sub>3</sub> (53) CH <sub>2</sub> =CHC(C <sub>3</sub> H <sub>7</sub> - <i>i</i> )(CN)OSi(CH <sub>3</sub> ) <sub>3</sub> (58)	427 427
C <sub>8</sub>	CH <sub>2</sub> =CHCH(CN)OCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub>	LDA, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -78°, 5 min	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> Br <i>n</i> -C <sub>6</sub> H <sub>13</sub> Br, -78°, 1-2 hr, then 0°, 1 hr	No reaction CH <sub>2</sub> =CHC(C <sub>6</sub> H <sub>13</sub> - <i>n</i> )(CN)OCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> (75)	427 33
94	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(CN)OSi(CH <sub>3</sub> ) <sub>3</sub>	LDA, THF, -78°, 2 hr	CH <sub>3</sub> I	CH <sub>2</sub> =C(CH <sub>3</sub> )CR(CN)OSi(CH <sub>3</sub> ) <sub>3</sub> A, R = CH <sub>3</sub> (80)	427
	CH <sub>3</sub> CH=CHCH(CN)OSi(CH <sub>3</sub> ) <sub>3</sub>	-35°, 8 hr LDA, THF, -78°, 2 hr	<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (67)	427
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (58)	427
			CH <sub>3</sub> I	CH <sub>3</sub> CH=CHCR(CN)OSi(CH <sub>3</sub> ) <sub>3</sub> A, R = CH <sub>3</sub> (87)	427
			<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> CH <sub>3</sub>	A, R = CH <sub>3</sub> (82)	427
			C <sub>2</sub> H <sub>5</sub> I	A, R = C <sub>2</sub> H <sub>5</sub> (85)	427
			<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br	A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (78)	427
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (73)	427
			<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> C <sub>4</sub> H <sub>9</sub> - <i>n</i>	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (62)	427
			CH <sub>2</sub> =CHCH <sub>2</sub> Br	A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (75)	427
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (76)	427			
Br(CH <sub>2</sub> ) <sub>2</sub> Br (0.5 eq)	A, R = CH <sub>2</sub> CH <sub>2</sub> Br (31)	427			
Br(CH <sub>2</sub> ) <sub>3</sub> Br (0.5 eq)	A, R = (CH <sub>2</sub> ) <sub>3</sub> Br (79)	427			
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (40)	427			
	A, R = CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (76)	427			
	LDA, THF, -35°, 5 hr -35°, 12 hr				
	LDA, THF, -35°, 12 hr	BrCH <sub>2</sub> - 	A, R = CH <sub>2</sub> -  (53)	427	
C <sub>9</sub>		LDA, THF, -78°, 5 min	CH <sub>3</sub> I	 A, R = CH <sub>3</sub> (92)	228a,312
	CH <sub>3</sub> CH=CHCH(CN)OCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub>	LDA, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -78°, 5 min	<i>i</i> -C <sub>3</sub> H <sub>7</sub> I C <sub>6</sub> H <sub>5</sub> COCH=CHC <sub>6</sub> H <sub>5</sub> , -78°, 5-10 min, then 0°	A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (80) C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )C(CN)(CH=CHCH <sub>3</sub> )OCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> (70-85)	228a,312 248
95		LDA, THF, -78°, 2 hr	CH <sub>3</sub> I		248
			<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	(CH <sub>3</sub> ) <sub>2</sub> C=CHCR(CN)OSi(CH <sub>3</sub> ) <sub>3</sub> A, R = CH <sub>3</sub> (88) A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (84)	427 427
	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH(CN)OSi(CH <sub>3</sub> ) <sub>3</sub>	LDA, THF, -78°, 2 hr	CH <sub>3</sub> I	C(CN)(CH=CHCH <sub>3</sub> )OCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> (70-85) (CH <sub>3</sub> ) <sub>2</sub> C=CHCR(CN)OSi(CH <sub>3</sub> ) <sub>3</sub> A, R = CH <sub>3</sub> (88) A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (84)	427 427
		LDA, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -78°, 5 min	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, -78°, 1-2 hr, then 0°, 1 hr	 (90)	33
		LDA, THF, -78°	CH <sub>3</sub> I, -78° to 25°, then hydrolysis	 (89)	228a
		LDA, THF, -78°, 5 min	CH <sub>3</sub> I	 A, R = CH <sub>3</sub> (80)	228a,312
		LDA, THF, -78°, 10 min	<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (78)	228a,312
			<i>i</i> -C <sub>3</sub> H <sub>7</sub> I, 2 hr	A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (78)	443
		LDA, THF, -78°, 10 min	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br, 2 hr	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (84)	443
			CH <sub>3</sub> I	A, R = CH <sub>3</sub> (84)	228a
	LDA, THF, -78°, 10 min		CR(CN)OSi(CH <sub>3</sub> ) <sub>3</sub>		
		CH <sub>3</sub> I, 2 hr	A, R = CH <sub>3</sub> (84)	228a,443	
		<i>i</i> -C <sub>3</sub> H <sub>7</sub> I, 2 hr	A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (80)	228a,443	
(CH <sub>3</sub> ) <sub>2</sub> C=CHCH(CN)OCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub>	LDA, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -78°		 (-)	493	

TABLE VI. CYANOHYDRIN ETHERS (Continued)

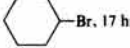

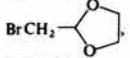





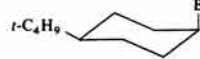





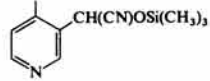

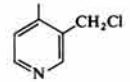
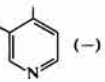
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>10</sub> (Contd.)	CH <sub>3</sub> CH=CHCH=CHCH(CN)OSi(CH <sub>3</sub> ) <sub>3</sub>	LDA, THF, -35°, 3 hr	CH <sub>3</sub> I	CH <sub>3</sub> CH=CHCH=CHCR(CN)OSi(CH <sub>3</sub> ) <sub>3</sub> A, R = CH <sub>3</sub> (97) A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (94)	427 427
C <sub>11</sub>	C <sub>6</sub> H <sub>5</sub> CH(CN)OCH <sub>2</sub> CH=CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CH(CN)OSi(CH <sub>3</sub> ) <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> ONa, <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH, 120°, 3 min LDA, THF, -78°, 5 min	— CH <sub>3</sub> I	CH <sub>3</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub> (-) C <sub>6</sub> H <sub>5</sub> CR(CN)OSi(CH <sub>3</sub> ) <sub>3</sub> A, R = CH <sub>3</sub> (-) A, R = CH <sub>3</sub> (80) A, R = CH <sub>3</sub> (92) A, R = C <sub>2</sub> H <sub>5</sub> (-) A, R = C <sub>2</sub> H <sub>5</sub> (85) A, R = C <sub>2</sub> H <sub>5</sub> (92) A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (-)	362 228a,312
			CH <sub>3</sub> OSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> , 2 hr (CH <sub>3</sub> O) <sub>2</sub> SO <sub>2</sub> , 1 hr C <sub>2</sub> H <sub>5</sub> I C <sub>2</sub> H <sub>5</sub> OSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> , 2 hr (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> SO <sub>2</sub> , 1 hr <i>i</i> -C <sub>3</sub> H <sub>7</sub> I <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> C <sub>3</sub> H <sub>7</sub> - <i>i</i> <i>i</i> -C <sub>4</sub> H <sub>9</sub> I <i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl, 1 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl, 24 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 1 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> I, 1 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> OSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> , 2 hr	228a,443 228a,443 228a,312 228a,443 228a,443 201,228a,312 228a 201,228a,312 228a,443 228a,443 228a,443	
		LDA, THF, -78°, 10 min	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl, 1 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl, 24 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 1 hr	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (22) A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (87) A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (72)	228a,443 228a,443 228a,443
		LDA, THF, -78°, 10 min	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I, 1 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> OSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> , 2 hr  Br, 17 hr	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (74) A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (91) A, R =  (48)	228a,443 228a,443 228a,443
			CH <sub>2</sub> =CHCH <sub>2</sub> Br, 1 hr C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> Br, 1.5 hr  Br, 7 hr Br(CH <sub>2</sub> ) <sub>3</sub> Cl BrCH <sub>2</sub> CH <sub>2</sub> Br (0.5 eq), 4 hr Br(CH <sub>2</sub> ) <sub>3</sub> Br (0.5 eq), 3 hr	A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (96) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (96) A, R = CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (62) A, R = CH <sub>2</sub>  (60) A, R = (CH <sub>2</sub> ) <sub>3</sub> Cl (85) A, R = CH <sub>2</sub> CH <sub>2</sub> Br (30) A, R = (CH <sub>2</sub> ) <sub>3</sub> Br (80)	228a,443 228a,312 228a,443 228a,443 228a,443 228a,443 228a,443
		LDA, THF, -78°	 -CH <sub>2</sub> Br  -CH <sub>2</sub> I	A, R =  -CH <sub>2</sub> (76) A, R =  -CH <sub>2</sub> (80)	228a 228a
		LDA, CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , -78°	<i>i</i> -C <sub>4</sub> H <sub>9</sub> I BrCH <sub>2</sub> CH <sub>2</sub> (OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CH <sub>3</sub> CHO	A, R = <i>i</i> -C <sub>4</sub> H <sub>9</sub> (75) A, R = CH <sub>2</sub> CH <sub>2</sub> (OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (20) C <sub>6</sub> H <sub>5</sub> COR A, R = CH(CH <sub>3</sub> )OSi(CH <sub>3</sub> ) <sub>3</sub> (98)	228a 228a 204,617
			<i>i</i> -C <sub>4</sub> H <sub>9</sub>  C <sub>2</sub> H <sub>5</sub> CHO <i>i</i> -C <sub>3</sub> H <sub>7</sub> CHO <i>i</i> -C <sub>4</sub> H <sub>9</sub> CHO <i>i</i> -C <sub>4</sub> H <sub>9</sub> CHO CH <sub>3</sub> COCH <sub>3</sub>	A, R = <i>i</i> -C <sub>4</sub> H <sub>9</sub>  (84) A, R = CH(C <sub>2</sub> H <sub>5</sub> )OSi(CH <sub>3</sub> ) <sub>3</sub> (91) A, R = CH(C <sub>3</sub> H <sub>7</sub> - <i>i</i> )OSi(CH <sub>3</sub> ) <sub>3</sub> (100) A, R = CH(C <sub>4</sub> H <sub>9</sub> - <i>i</i> )OSi(CH <sub>3</sub> ) <sub>3</sub> (96) A, R = CH(C <sub>4</sub> H <sub>9</sub> - <i>i</i> )OSi(CH <sub>3</sub> ) <sub>3</sub> (80) A, R = C(CH <sub>3</sub> ) <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> (98)	228a 204,617 204,617 204,617 617 204,617
			 	A, R =  OSi(CH <sub>3</sub> ) <sub>3</sub> (98) A, R =  OSi(CH <sub>3</sub> ) <sub>3</sub> (100)	204,617 204,617
			C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub> CHO, -78° to -50°, 3 hr	A, R = C[OSi(CH <sub>3</sub> ) <sub>3</sub> ](CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (100) A, R = C[OSi(CH <sub>3</sub> ) <sub>3</sub> ](C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (98) A, C <sub>6</sub> H <sub>5</sub> COC[OSi(CH <sub>3</sub> ) <sub>3</sub> ]R <sub>1</sub> R <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> C(CN)[OSi(CH <sub>3</sub> ) <sub>3</sub> ]C(OH)R <sub>1</sub> R <sub>2</sub> A: 75, B: 25, R <sub>1</sub> = H, R <sub>2</sub> = C <sub>2</sub> H <sub>5</sub> (-) A: 82, B: 18, R <sub>1</sub> = H, R <sub>2</sub> = <i>i</i> -C <sub>3</sub> H <sub>7</sub> (-)	204,617 204,617 617 617
		LDA, THF, -78°, 5 min	CH <sub>3</sub> I	 A, R = CH <sub>3</sub> (63) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (59)	312,617 312,617
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br 	A, R = CH <sub>2</sub>  (-)	312

TABLE VI. CYANOHYDRIN ETHERS (Continued)

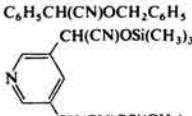
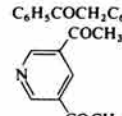
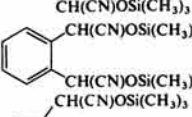
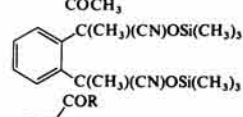
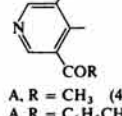
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>12</sub>	C <sub>6</sub> H <sub>5</sub> CH(CN)OCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub>	LDA, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -78°, 5 min	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br, -78°, 1-2 hr, then 0°, 1 hr	C <sub>6</sub> H <sub>5</sub> CR(CN)OCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (94)	33
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, -78°, 1-2 hr, then 0°, 1 hr	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (94)	33
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br, -78°, 1-2 hr, then 0°, 1 hr	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (71)	33
C <sub>13</sub>	C <sub>6</sub> H <sub>5</sub> CH=CHCH(CN)OSi(CH <sub>3</sub> ) <sub>3</sub>	LDA, THF, -78°, 5 min	CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> CH=CHCR(CN)OSi(CH <sub>3</sub> ) <sub>3</sub> A, R = CH <sub>3</sub> (-)	312
	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH(CN)OSi(CH <sub>3</sub> ) <sub>3</sub>	LDA, THF, -78°, 10 min	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br CH <sub>3</sub> I, 2 hr	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-) <i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> C(CH <sub>3</sub> )(CN)OSi(CH <sub>3</sub> ) <sub>3</sub> (93)	312 228a,443
	C <sub>6</sub> H <sub>5</sub> CH(CN)OTHP	NaH, CH <sub>3</sub> SOCH <sub>3</sub> , room temperature, 1.5 hr	<i>i</i> -C <sub>3</sub> H <sub>7</sub> I <i>n</i> -C <sub>7</sub> H <sub>15</sub> Br	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> C(C <sub>3</sub> H <sub>7</sub> - <i>i</i> )(CN)OSi(CH <sub>3</sub> ) <sub>3</sub> (90) C <sub>6</sub> H <sub>5</sub> CR(CN)OTHP A, R = C <sub>7</sub> H <sub>15</sub> - <i>n</i> (-)	228a 235
C <sub>15</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> ONa, <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH, 120°, 10 min	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> F <i>o,p</i> -(O <sub>2</sub> N) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> F	A, R = C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i> (-) A, R = C <sub>6</sub> H <sub>3</sub> (NO <sub>2</sub> ) <sub>2</sub> - <i>o,p</i> (-)	235 235
			LDA, THF, -30°	CH <sub>3</sub> I, then HCl, H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (30)  (75)
C <sub>16</sub>		LDA (2 eq), THF, -78°, 5 min	CH <sub>3</sub> I (2 eq)	 (80)	228a,312
			LDA, THF, -78°	CH <sub>3</sub> I (2 eq), -78° to 25°, then hydrolysis C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (2 eq)	 A, R = CH <sub>3</sub> (44) A, R = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (68)

TABLE VII. DITHIOLCARBAMATES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>6</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub>	LDA, THF,	CH <sub>3</sub> I	CH <sub>2</sub> =CHCHRSC(S)N(CH <sub>3</sub> ) <sub>2</sub> A, R = CH <sub>3</sub> (>96)	48, 313 515	
			C <sub>2</sub> H <sub>5</sub> I	A, R = C <sub>2</sub> H <sub>5</sub> (93)	48, 138	
			<i>n</i> -C <sub>3</sub> H <sub>7</sub> I	A, R = C <sub>3</sub> H <sub>7-n</sub> (>96)	48	
			<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	A, R = C <sub>3</sub> H <sub>7-i</sub> (>90)	48	
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	A, R = C <sub>4</sub> H <sub>9-n</sub> (96)	48, 138	
			<i>n</i> -C <sub>5</sub> H <sub>11</sub> I	A, R = C <sub>5</sub> H <sub>11-n</sub> (>93)	313	
			<i>n</i> -C <sub>6</sub> H <sub>13</sub> I	A, R = C <sub>6</sub> H <sub>13-n</sub> (94)	138	
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (>91)	48, 515	
			CH <sub>3</sub> SSCH <sub>3</sub>	A, R = SCH <sub>3</sub> (>88)	313	
			C <sub>7</sub>	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub>	LDA, THF, -55°, -60°	H <sub>2</sub> O
CH <sub>3</sub> I	A, R = CH <sub>3</sub> (98)	48, 218				
C <sub>2</sub> H <sub>5</sub> I	A, R = C <sub>2</sub> H <sub>5</sub> (>90)	48				
CH <sub>3</sub> OCH <sub>2</sub> Cl	A, R = CH <sub>2</sub> OCH <sub>3</sub> (>84)	48				
<i>n</i> -C <sub>3</sub> H <sub>7</sub> I	A, R = C <sub>3</sub> H <sub>7-n</sub> (>88)	48				
<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	A, R = C <sub>3</sub> H <sub>7-i</sub> (>82)	48				
<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	A, R = C <sub>4</sub> H <sub>9-n</sub> (>92)	48				
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (>85)	515				
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> CH <sub>3-p</sub> (-)	515				
CH <sub>3</sub> SSCH <sub>3</sub>	A, R = SCH <sub>3</sub> (>90)	313, 515				
LDA, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO-THF, 1:1, -60°, 10 min	H <sub>2</sub> O	A, CH <sub>2</sub> =C(CH <sub>3</sub> )CH(SH)C(S)N(CH <sub>3</sub> ) <sub>2</sub> + B, CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub> A: 98, B: 2 (97.5)				218
LDA, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO-THF, 1:3, -60°, 30 min	CH <sub>3</sub> I	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(SCH <sub>3</sub> )C(S)N(CH <sub>3</sub> ) <sub>2</sub> (96)				218
CH <sub>3</sub> CH=CHCH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub> <i>trans</i>	LDA, THF, -55°	CH <sub>3</sub> I				CH <sub>3</sub> CH=CHCHRSC(S)N(CH <sub>3</sub> ) <sub>2</sub> <i>trans</i> A, R = CH <sub>3</sub> (>88)
		C <sub>2</sub> H <sub>5</sub> I	A, R = C <sub>2</sub> H <sub>5</sub> (>86)	48		
CH <sub>3</sub> CH=CHCH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub>	LDA, THF, -78°	CH <sub>2</sub> =CHCH <sub>2</sub> Cl	A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (>95)	48		
		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (>85)	515		
		CH <sub>3</sub> SSCH <sub>3</sub>	CH <sub>3</sub> CH=CHCH(SCH <sub>3</sub> )SC(S)N(CH <sub>3</sub> ) <sub>2</sub> (>95)	313		

TABLE VII. DITHIOCARBAMATES (Continued)

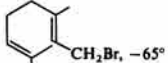


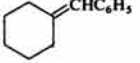
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>7</sub> (Contd.)	CH <sub>2</sub> =C(OCH <sub>3</sub> )CH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub>	LDA, THF, -78°	n-C <sub>5</sub> H <sub>11</sub> I, -65°	A, CH <sub>2</sub> =CH(OCH <sub>3</sub> )CHRSC(S)N(CH <sub>3</sub> ) <sub>2</sub> + B, RCH <sub>2</sub> C(OCH <sub>3</sub> )=CHSC(S)N(CH <sub>3</sub> ) <sub>2</sub> A: 98, B: 2, R = C <sub>5</sub> H <sub>11-n</sub> (97)	298	
			(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Br, -65°	A: 98, B: 2, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (99)	298	
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br, -65°	A: 98, B: 2, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (98)	298	
			 CH <sub>2</sub> Br, -65°	A: 98, B: 2, R = CH <sub>2</sub> (98)	298	
			n-C <sub>6</sub> H <sub>13</sub> CHCH <sub>2</sub> , -65°	A: 15, B: 85, R = CH <sub>2</sub> CH(OH)C <sub>6</sub> H <sub>13-n</sub> (63)	298	
			C <sub>6</sub> H <sub>5</sub> CHO, -65°	A: 17, B: 83, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (98)	298	
			CH <sub>3</sub> COCH <sub>3</sub> , -65°	A: 20, B: 80, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (96)	298	
			 COCH <sub>3</sub> , -65°	A: 20, B: 80, R = C(OH)(CH <sub>3</sub> ) (96)	298	
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> , -65°	A: 20, B: 80, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (97)	298	
			n-C <sub>5</sub> H <sub>11</sub> I	CH <sub>3</sub> SCH=CHCH(SC(S)N(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub> (>69)	313	
C <sub>8</sub>	CH <sub>3</sub> SCH=CHCH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub> <i>trans</i> CH <sub>3</sub> SCH=C(CH <sub>3</sub> )CH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub>	LDA, THF, -78° LICA, THF, -55° LDA, THF, -78°, then -55°	I(CH <sub>2</sub> ) <sub>4</sub> OTHP	C <sub>2</sub> H <sub>5</sub> CH=CHCH[SC(S)N(CH <sub>3</sub> ) <sub>2</sub> ](CH <sub>2</sub> ) <sub>4</sub> OTHP <i>trans</i> (90-93)	138	
			n-C <sub>5</sub> H <sub>11</sub> I	CH <sub>3</sub> SCH=C(CH <sub>3</sub> )CHRSC(S)N(CH <sub>3</sub> ) <sub>2</sub> A, R = C <sub>5</sub> H <sub>11-n</sub> (67)	313	
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-)	313	
			p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -p (-)	515	
C <sub>10</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub>	LDA, THF, -60°, 5 min LDA, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO-THF, 1:1, -60°, 60 min	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CHRSC(S)N(CH <sub>3</sub> ) <sub>2</sub> A, R = H (99)	218	
			CH <sub>3</sub> I H <sub>2</sub> O	A, R = CH <sub>3</sub> (99) C <sub>6</sub> H <sub>5</sub> CH(SH)C(S)N(CH <sub>3</sub> ) <sub>2</sub> (96)	218 218	
C <sub>11</sub>	n-C <sub>4</sub> H <sub>9</sub> CH=CHCH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub> <i>trans</i>	LICA, THF, -55°	CH <sub>3</sub> I I(CH <sub>2</sub> ) <sub>5</sub> OTHP	C <sub>6</sub> H <sub>5</sub> CH(SCH <sub>3</sub> )C(S)N(CH <sub>3</sub> ) <sub>2</sub> (96) n-C <sub>4</sub> H <sub>9</sub> CH=CHCH[SC(S)N(CH <sub>3</sub> ) <sub>2</sub> ](CH <sub>2</sub> ) <sub>5</sub> OTHP <i>trans</i> (90-93)	218 138	
C <sub>11</sub>	n-C <sub>5</sub> H <sub>11</sub> CH=CHCH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub>	LDA, THF, -78°	CH <sub>3</sub> SSCH <sub>3</sub>	n-C <sub>5</sub> H <sub>11</sub> CH=CHCH(SCH <sub>3</sub> )SC(S)N(CH <sub>3</sub> ) <sub>2</sub> (78)	313	
C <sub>12</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub>	LDA, THF, -78°	C <sub>2</sub> H <sub>5</sub> CHO, -78°, 1 hr, then H <sub>2</sub> O*	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC(S)SCH(C <sub>6</sub> H <sub>5</sub> )CH(OH)C <sub>2</sub> H <sub>5</sub> (95)	447	
C <sub>13</sub>	n-C <sub>5</sub> H <sub>11</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub> n-C <sub>6</sub> H <sub>13</sub> CH=CHCH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub> <i>trans</i> n-C <sub>4</sub> H <sub>9</sub> CH=CHCH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH=CHCH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub> n-C <sub>4</sub> H <sub>9</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> SC(S)N(CH <sub>3</sub> ) <sub>2</sub>	LDA, THF, -78° LICA, THF, -55° LDA, THF, -55°, 10 min LDA, THF, -78° LDA, THF, -55°, 10 min LDA, THF, -55°, 10 min LDA, THF, -55°, 10 min LDA, THF, -55°, 10 min	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 25-60°		 (78)	447
			CH <sub>3</sub> SSCH <sub>3</sub> I(CH <sub>2</sub> ) <sub>5</sub> OTHP	n-C <sub>5</sub> H <sub>11</sub> CH=C(CH <sub>3</sub> )CH(SCH <sub>3</sub> )SC(S)N(CH <sub>3</sub> ) <sub>2</sub> (>69) n-C <sub>6</sub> H <sub>13</sub> CH=CHCH[SC(S)N(CH <sub>3</sub> ) <sub>2</sub> ](CH <sub>2</sub> ) <sub>5</sub> OTHP (90-93)	313 138	
			[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCSS] <sub>2</sub> , -60°, 1 hr	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC(S)SCH(C <sub>4</sub> H <sub>9-n</sub> )CH=CHSC(S)N(CH <sub>3</sub> ) <sub>2</sub> (-)	139	
			CH <sub>3</sub> SSCH <sub>3</sub>	n-C <sub>4</sub> H <sub>9</sub> CH <sub>2</sub> CH=CHCH(SCH <sub>3</sub> )SC(S)N(CH <sub>3</sub> ) <sub>2</sub> (>60)	313	
			[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCSS] <sub>2</sub> , -60°, 1 hr	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC(S)SCH(C <sub>4</sub> H <sub>9-n</sub> )C(CH <sub>3</sub> )=CHSC(S)N(CH <sub>3</sub> ) <sub>2</sub> (-)	139	
			[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCSS] <sub>2</sub> , -60°, 1 hr	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC(S)SCH(C <sub>6</sub> H <sub>5</sub> )CH=CHSC(S)N(CH <sub>3</sub> ) <sub>2</sub> (-)	139	
			[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCSS] <sub>2</sub> , -60°, 1 hr	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC(S)SCH(C <sub>6</sub> H <sub>17-n</sub> )CH=CHSC(S)N(CH <sub>3</sub> ) <sub>2</sub> (-)	139	
			CH <sub>3</sub> SSCH <sub>3</sub>	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH(SCH <sub>3</sub> )SC(S)N(CH <sub>3</sub> ) <sub>2</sub> (-)	515	

TABLE VIII. DITHIOESTERS

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>6</sub>	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SC(S)CH <sub>3</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, -78°, 30 min	<i>n</i> -C <sub>8</sub> H <sub>17</sub> Br (1 eq), then CH <sub>3</sub> I (1 eq), -25°	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(C <sub>8</sub> H <sub>17-n</sub> )SC(SCH <sub>3</sub> )=CH <sub>2</sub> (unstable)	45
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (1 eq), then CH <sub>3</sub> I (1 eq), -25°	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )SC(SCH <sub>3</sub> )=CH <sub>2</sub> (unstable)	45
102 C <sub>8</sub>	C <sub>6</sub> H <sub>5</sub> C(S)SCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> MgBr, THF, -17°, 45 min <i>i</i> -C <sub>3</sub> H <sub>7</sub> MgBr, THF, -17°, 45 min CH <sub>3</sub> MgBr, THF, -20°, 1 hr, then reflux, 18 hr	CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )(SCH <sub>3</sub> )SC <sub>2</sub> H <sub>5</sub> (80)	163
			CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )(SCH <sub>3</sub> )SC <sub>3</sub> H <sub>7-i</sub> (80)	163
			H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> C(SCH <sub>3</sub> )=C(SCH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> ( <i>E</i> ) and ( <i>Z</i> ) (-)	163
C <sub>13</sub>	C <sub>6</sub> H <sub>5</sub> C(S)SC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> Li, ether, -78°, 10 min C <sub>6</sub> H <sub>5</sub> Li, ether, room temperature, 10 min	CH <sub>3</sub> OH	C <sub>6</sub> H <sub>5</sub> CH(SC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (49)	162
			CH <sub>3</sub> OH	C <sub>6</sub> H <sub>5</sub> CH(SC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (34) + C <sub>6</sub> H <sub>5</sub> C(SC <sub>6</sub> H <sub>5</sub> )=C(SC <sub>6</sub> H <sub>5</sub> )C <sub>6</sub> H <sub>5</sub> (19)	162

TABLE IX. DITHIOKETALS

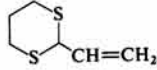
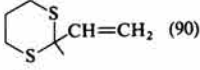


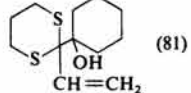
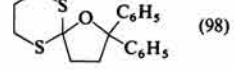
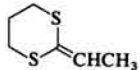
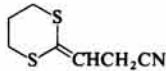
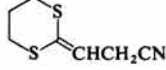
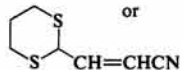
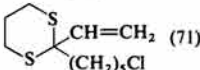
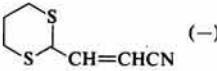
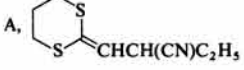
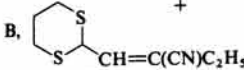
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>6</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78° to 0°	CH <sub>3</sub> I	 (90)	9
			C <sub>6</sub> H <sub>5</sub> CHO	 (90)	9
				 (81)	9
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	 (98)	9
C <sub>7</sub>	   or 	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -20°	I(CH <sub>2</sub> ) <sub>3</sub> Cl, -45° to -25°	 (71)  (-)	368 507
			C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH, -20°, 30 min	CH <sub>3</sub> CO <sub>2</sub> H	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	C <sub>2</sub> H <sub>5</sub> I, -78°, 1 hr	A, 	507
				B,  + A: 95, B: 5 (74)	

TABLE IX. DITHIOKETALS (Continued)

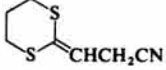
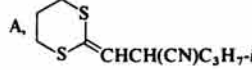
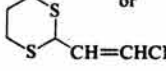
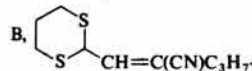
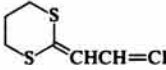
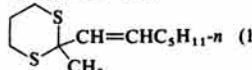
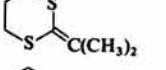
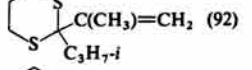
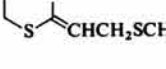
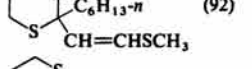
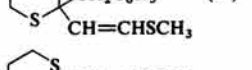
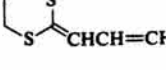
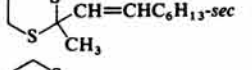
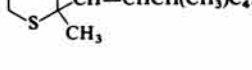
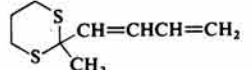
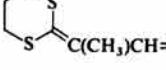
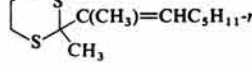
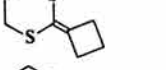
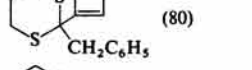
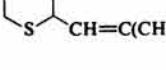
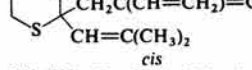
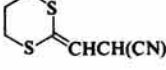
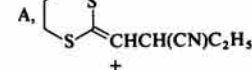
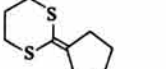
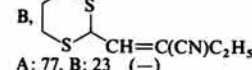
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>7</sub> (Contd.)		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br, -78° to room temperature	A,  +	507	
	or 			B,  A: 81, B: 19 (31)		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80°	CH <sub>3</sub> I	 (100)	164	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -78°	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Cl	 (92)	109	
		LDA, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, THF, -78°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I	 (92)	382	
104			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	 (94)	382	
	C <sub>8</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80°	CH <sub>3</sub> I	 (100)	164
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80°	CH <sub>3</sub> I	 (not isolated)	164
		LDA, THF, -80°	CH <sub>3</sub> I	 (100)	164	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80°	CH <sub>3</sub> I	 (not isolated)	164	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	 (80)	109	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -20°, 6 hr	CH <sub>2</sub> =CHC(CH <sub>2</sub> Br)=CH <sub>2</sub> , <i>cis</i> NaI	 (28)	548	
	CH <sub>3</sub> C≡CCH(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> ONa (cat), NH <sub>3</sub> (liq), 20 min	H <sub>2</sub> O	CH <sub>3</sub> CH=C=C(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (-)	281	
		C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OD, 20°	H <sub>2</sub> O	CH <sub>3</sub> CD=C=C(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (-)	281	
		LiNH <sub>2</sub> , NH <sub>3</sub> (liq), 1 min	H <sub>2</sub> O	A, CH <sub>3</sub> CR=C=C(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> +	281	
105		LiNH <sub>2</sub> , NH <sub>3</sub> (liq)-THF, 5:1, -30°, 1 min	CH <sub>3</sub> I	B, CH <sub>3</sub> C≡CCR(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> A: 40, B: 60, R = H (-)	281	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether-THF, 1:2, -65°, 1 min	CH <sub>3</sub> I	A (trace), B (58), R = CH <sub>3</sub>	281	
				A (0), B (78), R = CH <sub>3</sub>	281	
C <sub>9</sub>		C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH, -20°, 30 min	CH <sub>3</sub> CO <sub>2</sub> H	A,  +	507	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO	<i>n</i> -C <sub>7</sub> H <sub>15</sub> I	B,  A: 77, B: 23 (-)	109	



TABLE IX. DITHIOKETALS (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.		
C <sub>9</sub> (Contd.)		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO	CH <sub>3</sub> I		109		
			<i>i</i> -C <sub>3</sub> H <sub>7</sub> Cl	A, R = CH <sub>3</sub> (87) A, R = C <sub>3</sub> H <sub>7-<i>i</i></sub> (80)	109		
106		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO	CH <sub>3</sub> I		109		
			LDA, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, THF, -78°	CH <sub>3</sub> OH	A, R = CH <sub>3</sub> (90) A, R = H (86)	382	
			CH <sub>3</sub> I	A, R = CH <sub>3</sub> (88)	382		
			<i>n</i> -C <sub>6</sub> H <sub>13</sub> I	A, R = C <sub>6</sub> H <sub>13-n</sub> (81)	382		
	C <sub>2</sub> H <sub>5</sub> C≡CCH(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -33°, 1 min	CH <sub>3</sub> SSCH <sub>3</sub>	A,	382		
			B,	A: 1, B: 1 (65) A, C <sub>2</sub> H <sub>5</sub> C≡CCH(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> + B, C <sub>2</sub> H <sub>5</sub> CH=C=C(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	281		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether-THF, 1:2, -65°, 1 min	H <sub>2</sub> O	A: 53, B: 47 (-) A: 36, B: 64 (-)	281		
			C <sub>2</sub> H <sub>5</sub> ONa (cat), NH <sub>3</sub> (liq), 20 min LiNH <sub>2</sub> , NH <sub>3</sub> (liq), 1 min	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> CH=C=C(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (-) A, C <sub>2</sub> H <sub>5</sub> C≡CCH(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> + B, C <sub>2</sub> H <sub>5</sub> CH=C=C(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	281	
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 1 min KNH <sub>2</sub> , NH <sub>3</sub> (liq), 1 min	H <sub>2</sub> O	A: 70, B: 30 (-) A: 40, B: 60 (-)	281		
			H <sub>2</sub> O	A: 30, B: 70 (-)	281		
107	CH <sub>3</sub> OC(CH <sub>3</sub> ) <sub>2</sub> C≡CCH(SCH <sub>3</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -50°, 35 min	CH <sub>3</sub> I	A, C <sub>2</sub> H <sub>5</sub> C≡CCR(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> + B, C <sub>2</sub> H <sub>5</sub> R=C=C(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	281		
			<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	A: (66), B: (trace), R = CH <sub>3</sub>	281		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	CH <sub>2</sub> =CHCH <sub>2</sub> Br	A: (78), B: (trace), R = CH <sub>2</sub> CH=CH <sub>2</sub>	281		
			CH <sub>3</sub> OCH <sub>2</sub> Cl	A: (71), B: (0), R = CH <sub>2</sub> OCH <sub>3</sub>	281		
			CH <sub>3</sub> COCH <sub>3</sub>	A: (82), B: (0), R = C(OH)(CH <sub>3</sub> ) <sub>2</sub>	281		
			H <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=C=C=C(SCH <sub>3</sub> ) <sub>2</sub> (75)	170		
				<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 0°, then 25°, 2 hr		(-)	399
						(33)	600
					"	(63)	600
					"	(28)	600
2-Phenylquinoline, K, THF, 20°, 3 hr	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 0°, then 25°, 2 hr	"	(28)	600			
2-Phenylpyridine, K, THF, 20°, 3 hr	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 0°, then 25°, 2 hr	"	(50)	600			
2,6-Diphenylpyridine, K, THF, 20°, 3 hr	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 0°, then 25°, 2 hr	"	(52)	600			
2,4,6-Triphenylpyridine, K, THF, 20°, 3 hr	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 0°, then 25°, 2 hr	"	(16)	600			
2-[2-Pyridyl]pyridine, K, THF, 20°, 3 hr	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 0°, then 25°, 2 hr	"	(25)	600			
2,4,6-Triphenyltriazine, K, THF, 20°, 3 hr	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 0°, then 25°, 2 hr	"	(25)	600			

TABLE IX. DITHIOKETALS (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>10</sub> (Contd.)		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.2 eq), C <sub>6</sub> H <sub>14</sub> , THF, -78°, 2 hr	CH <sub>3</sub> SSCH <sub>3</sub>		A, R = SCH <sub>3</sub> (95)	258
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -60°, 1 hr	(CH <sub>3</sub> ) <sub>3</sub> SiCl, -30° to -15°	A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (90)	377	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.05 eq), THF, -40°, then -25° to -15°, 1.5-2.5 hr	<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	A, R = C <sub>3</sub> H <sub>7-<i>i</i></sub> (97)	573	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), THF, -30°, 1 hr	<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	" (90)	224	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78° to 0°	<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	" (86)	9	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -60° to -75°, 1 hr, then -50°, 6 hr	D <sub>2</sub> O	A, R = D (95)	571	
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -40°, 1 hr	0°, 10 days	A, R =  (75)	335
			0°, 2.5 days	A, R =  (95)	335	
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	BrC <sub>6</sub> H <sub>3</sub> (NO <sub>2</sub> ) <sub>2</sub> - <i>o,p</i> , -20°, 2 hr, then 0°, 1 hr	A, R =  (-)	336
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, -30°, 30 min		CO <sub>2</sub> , 2 hr	A, R =  (50)	336
A, R = CO <sub>2</sub> H (-)	414					
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 1 hr		-78°, 2 hr, then room temperature	A, R =  (54)	527		
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -25°, 1.5 hr		Si(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> )Cl	A, R =  (78)	240		
		(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCl, 0°	A, R = Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (66)	240		
		(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> GeBr, 0°, then room temperature, 20 hr	A, R = Ge(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (70)	240		
		(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnCl	A, R = Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (79)	240		
		C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	A, R = C <sub>2</sub> H <sub>5</sub> (92)	229		
		C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> C <sub>3</sub> H <sub>7-<i>n</i></sub>	A, R = C <sub>3</sub> H <sub>7-<i>n</i></sub> (87)	229		
		<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> C <sub>3</sub> H <sub>7-<i>n</i></sub>	A, R = C <sub>3</sub> H <sub>7-<i>n</i></sub> (85)	229		
		C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> C <sub>4</sub> H <sub>9-<i>n</i></sub>	A, R = C <sub>4</sub> H <sub>9-<i>n</i></sub> (89)	229		
		C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> C <sub>8</sub> H <sub>17-<i>n</i></sub>	A, R = C <sub>8</sub> H <sub>17-<i>n</i></sub> (90)	229		
		<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CHNO <sub>2</sub> , -78°	A, R = CH(CH <sub>2</sub> NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> (90)	572,575		
<i>o,o'</i> -(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH=CHNO <sub>2</sub> ,	A, R = CH(CH <sub>2</sub> NO <sub>2</sub> )C <sub>6</sub> H <sub>3</sub> (OCH <sub>3</sub> ) <sub>2</sub> - <i>o,o'</i> (72)	572,575				
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80°		H <sub>2</sub> O	A, R = H (-)	164		
		D <sub>2</sub> O	A, R = D (-)	164		
		CH <sub>3</sub> I	A, R = CH <sub>3</sub> (-)	164		

TABLE IX. DITHIOKETALS (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>10</sub> (Contd.)		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>5</sub> H <sub>12</sub> , DDB, -80°	CH <sub>3</sub> I, hydrolysis	 $\alpha_D = -1.8^\circ$	4, 575
110		LDA, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, THF, -78°	CH <sub>3</sub> I	A,	382
			CH <sub>3</sub> OH	 A: 1, B: 5 (78) (73)	382
111		LDA, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, THF, -78°	CH <sub>3</sub> OH		382
			CH <sub>3</sub> I	A, R = H (93)	109,382
			CH <sub>2</sub> =CHCH <sub>2</sub> Br	A, R = CH <sub>3</sub> (74-87) A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (86)	382
C <sub>11</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°		A, R = CH(CH <sub>2</sub> NO <sub>2</sub> )-	(35.5) 574
					(-) 399
				 A, R =	(88) 249
				A, R = CH(CH <sub>2</sub> NO <sub>2</sub> )-	(70) 574
111		LDA, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, THF, -78°	CH <sub>3</sub> I		(81) 382
			CH <sub>2</sub> =CHCH <sub>2</sub> Br	A, CH <sub>2</sub> CH=CH <sub>2</sub>	382
				B, CH <sub>2</sub> CH=CH <sub>2</sub>	A: 1.7, B: 1 (82)
C <sub>6</sub> H <sub>5</sub> CH(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>		NaNH <sub>2</sub> (1 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 0°, then room temperature, 8 hr	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 50°, 3 hr	C <sub>6</sub> H <sub>5</sub> C(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (35) + C <sub>6</sub> H <sub>5</sub> CH(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (33)	110
		NaNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq)	C <sub>2</sub> H <sub>5</sub> Br (2 eq), overnight, room temperature	<i>n</i> -C <sub>4</sub> H <sub>9</sub> SC <sub>2</sub> H <sub>5</sub> (-) C <sub>6</sub> H <sub>5</sub> C(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> R A, R = C <sub>2</sub> H <sub>5</sub> (87)	49

TABLE IX. DITHIOKETALS (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>11</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CH(SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>		<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br <i>n</i> -C <sub>4</sub> H <sub>9</sub> Br <i>sec</i> -C <sub>4</sub> H <sub>9</sub> Br C <sub>2</sub> H <sub>5</sub> SSC <sub>2</sub> H <sub>5</sub>	A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (80) A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (85) A, R = C <sub>4</sub> H <sub>9</sub> - <i>sec</i> (84) A, R = SC <sub>2</sub> H <sub>5</sub> (76)	49 49 49 49
		C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> CO <sub>2</sub> H	A, + B,	507
C <sub>12</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, 110°	—	A, + B,	A: 82, B: 18 (-)
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OD, 110°	—	A, + B,	A: 1, B: 2, R = H (-) A: 1, B: 2, R = D (-)
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.2 eq), C <sub>6</sub> H <sub>14</sub> , THF, -78°, 2 hr	CH <sub>3</sub> I CH <sub>3</sub> SSCH <sub>3</sub>	—	A: 1, B: 1, R = CH <sub>3</sub> (-) A: 1, B: 0, R = SCH <sub>3</sub> (-)	370 258
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30° to -20°, 1 hr	D <sub>2</sub> O CH <sub>3</sub> I CH <sub>3</sub> OTs (CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> (CH <sub>3</sub> ) <sub>3</sub> SiCl	—	A: 100, B: 0, R = D (70) A: 56, B: 44, R = CH <sub>3</sub> (60) A: 82, B: 18, R = CH <sub>3</sub> (80) A: 100, B: 0, R = CH <sub>3</sub> (55) A: 100, B: 0, R = (CH <sub>3</sub> ) <sub>3</sub> Si (72)	231b 231b 231b 231b 231b
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, 110°	—	A: 63, B: 37, R = C <sub>3</sub> H <sub>7</sub> - <i>n</i> (79) A: 73, B: 27, R = C <sub>3</sub> H <sub>7</sub> - <i>n</i> (57) A: 26, B: 74, R = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (74) A: 22, B: 78, R = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (66) A: 14, B: 86, R = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (75) A: 10, B: 90, R = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (60) A: 10, B: 90, R = <i>m</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> (69)	231b 231b 231b 231b 231b 231b 231b
C <sub>13</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, 110°	—	A, + B,	370
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	D <sub>2</sub> O, DCl		(100)
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>12</sub> , THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO	D <sub>2</sub> O, DCl	A, + B,	399 399
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -35°, 1.5 hr	Br(CH <sub>2</sub> ) <sub>4</sub> Br		(77)
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -35°, 1.5 hr	Br(CH <sub>2</sub> ) <sub>3</sub> Br, -10°, 2 hr		(65)

TABLE IX. DITHIOKETAL (Continued)

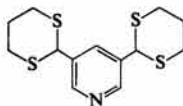
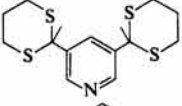
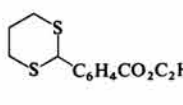
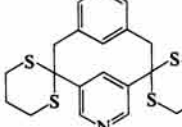
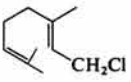
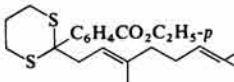
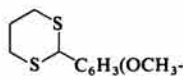
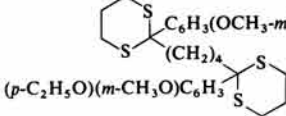
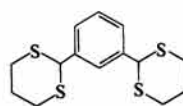
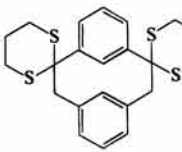
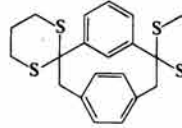
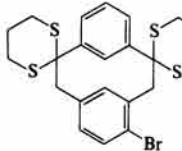
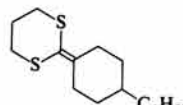
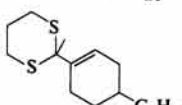
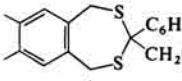
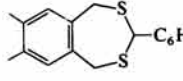
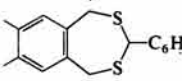
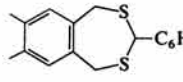
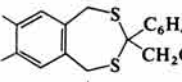
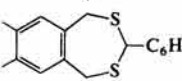
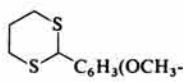
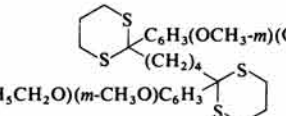

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>13</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, LiBr, THF, -40°	CH <sub>3</sub> I	 (90)	120
114		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	BrCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br- <i>m</i>	 (10)	120
				 C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> - <i>p</i> (-)	399
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -35°, 1.5 hr	Br(CH <sub>2</sub> ) <sub>4</sub> Br, -10°, 2 hr	 C <sub>6</sub> H <sub>3</sub> (OCH <sub>3</sub> - <i>m</i> )(OC <sub>2</sub> H <sub>5</sub> - <i>p</i> ) (CH <sub>2</sub> ) <sub>4</sub> (78)	404
C <sub>14</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, -30°	BrCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br- <i>m</i>	 (64-76)	119
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, reflux, high-dilution technique	BrCH <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> Br- <i>p</i>	 (36)
			BrC <sub>6</sub> H <sub>3</sub> (CH <sub>2</sub> Br) <sub>2</sub> - <i>o,p</i>	 (52)	456
115		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -20°	CH <sub>3</sub> I	 C <sub>4</sub> H <sub>9</sub> - <i>t</i> (77)	109
			CH <sub>2</sub> CHCH <sub>2</sub> F, -20°, then 0°, 7 days	 C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> F (48)	419
C <sub>17</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -20°	CH <sub>2</sub> CHCH <sub>2</sub> F, -20°, then 0°, 7 days	 C <sub>6</sub> H <sub>5</sub> (25)	
C <sub>18</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -20°	CH <sub>2</sub> CHCH <sub>2</sub> F, -20°, then 0°, 7 days	 C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> CH <sub>2</sub> CH(OH)CH <sub>2</sub> F (43)	419
			 C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (23)		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -35°, 1.5 hr	Br(CH <sub>2</sub> ) <sub>4</sub> Br, -10°, 2 hr	 C <sub>6</sub> H <sub>3</sub> (OCH <sub>3</sub> - <i>m</i> )(OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> - <i>p</i> ) (CH <sub>2</sub> ) <sub>4</sub> (45)	404
				 (p-C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O)( <i>m</i> -CH <sub>3</sub> O)C <sub>6</sub> H <sub>3</sub> (45)	

TABLE IX. DITHIOKETALS (Continued)

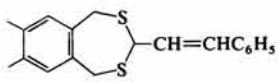
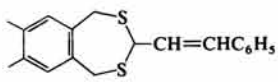
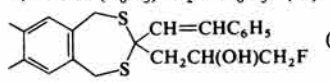
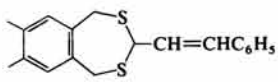
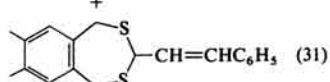
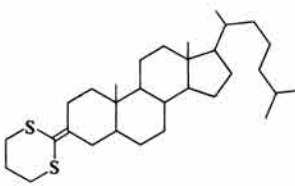
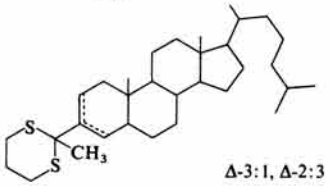
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.			
C <sub>19</sub>		NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, 0°  NaH (1 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO-THF, 2:1, 0°, then 15-17°, overnight <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 1 hr CuI (0.5 eq), -78°, 1 hr  <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -20°	CH <sub>3</sub> I, 6 hr	C <sub>6</sub> H <sub>5</sub> CR(SC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> A, R = CH <sub>3</sub> (63) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (38) A, R = CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (-) A, R = CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (-) A, R = COC <sub>6</sub> H <sub>5</sub> (38) A, R = CH <sub>3</sub> (66)	153 153 153 153 153 110			
			CH <sub>2</sub> =CHCOCH <sub>3</sub>	A, R = CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (94)	251			
			(CH <sub>3</sub> ) <sub>2</sub> C=CHCOCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> CH=CHCOCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub>	A, R = C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (82) A, R = CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> COCH <sub>3</sub> (94) A, R = CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (94)	251 251 251			
				CH <sub>2</sub> CHCH <sub>2</sub> F, -20°, then 0°, 7 days	 (52)	557		
				 (31)				
			C <sub>31</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO	CH <sub>3</sub> I		109
						Δ-3:1, Δ-2:3 (75)		

TABLE X. ETHERS



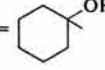


No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>4</sub>	HC≡CCH <sub>2</sub> OCH <sub>3</sub>	CH <sub>3</sub> ONa, CH <sub>3</sub> SOCH <sub>3</sub> , 90°, 15 min	—	CH <sub>2</sub> =C=CHOCH <sub>3</sub> (32)	428	
		CH <sub>3</sub> SOCH <sub>2</sub> Na, CH <sub>3</sub> SOCH <sub>3</sub> , room temperature, 10 hr.	—	A, CH <sub>2</sub> =C=CHOCH <sub>3</sub> + B, HC≡CCH <sub>2</sub> OCH <sub>3</sub> A: 50, B: 50 (—) A: 100, B: 1 (—)	428	
	CH <sub>2</sub> =C=CHOCH <sub>3</sub>	3 days	—	—	—	—
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), neat, 70°, 2-3 hr	—	—	CH <sub>2</sub> =C=CHOCH <sub>3</sub> (82)	432
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -25°, 10 min	CH <sub>3</sub> COCH <sub>3</sub> , -25°, 20 min	CH <sub>3</sub> COCH <sub>3</sub> , -25°, 20 min	CH <sub>2</sub> =C=C(OCH <sub>3</sub> )R A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (82)	431
			C <sub>2</sub> H <sub>5</sub> COC <sub>2</sub> H <sub>5</sub> , -25°, 20 min	C <sub>2</sub> H <sub>5</sub> COC <sub>2</sub> H <sub>5</sub> , -25°, 20 min	A, R = C(OH)(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (84)	431
			CH <sub>3</sub> CHO, -25°, 20 min	CH <sub>3</sub> CHO, -25°, 20 min	A, R = CH(OH)CH <sub>3</sub> (80)	431
			C <sub>2</sub> H <sub>5</sub> CHO, -25°, 20 min	C <sub>2</sub> H <sub>5</sub> CHO, -25°, 20 min	A, R = CH(OH)C <sub>2</sub> H <sub>5</sub> (80)	431
					A, R =  (88)	431
			-25°, 20 min	CH <sub>3</sub> SSCH <sub>3</sub> , -40°	A, R = SCH <sub>3</sub> (75)	431
			ClCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> , -30°, 1 hr	ClCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> , -30°, 1 hr	A, R = CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> (78)	433
			ClCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> , -30°, 1 hr	ClCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> , -30°, 1 hr	A, R = CH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> (79)	433
			ClCH(C <sub>2</sub> H <sub>5</sub> )OC <sub>2</sub> H <sub>5</sub> , -30°, 1 hr	ClCH(C <sub>2</sub> H <sub>5</sub> )OC <sub>2</sub> H <sub>5</sub> , -30°, 1 hr	A, R = CH(C <sub>2</sub> H <sub>5</sub> )OC <sub>2</sub> H <sub>5</sub> (85)	433
			CH <sub>2</sub> O (gas), 1 hr	CH <sub>2</sub> O (gas), 1 hr	A, R = CH <sub>2</sub> OH (70)	316
			CH <sub>2</sub> CH <sub>2</sub> , -50°,  then -15°, 2 hr	CH <sub>2</sub> CH <sub>2</sub> , -50°,  then -15°, 2 hr	A, R = CH <sub>2</sub> CH <sub>2</sub> OH (72)	316

TABLE X. ETHERS (Continued)

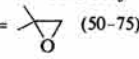
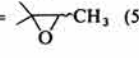
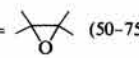
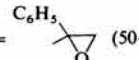
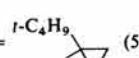


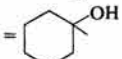

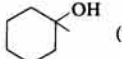
No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>4</sub> (Contd.)	CH <sub>2</sub> =C=CHOCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-ether, 1:1, -20°, 10 min	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, -20°, 4 hr <i>n</i> -C <sub>3</sub> H <sub>7</sub> Br, -20°, 4 hr <i>i</i> -C <sub>3</sub> H <sub>7</sub> I, -20°, 4 hr <i>n</i> -C <sub>3</sub> H <sub>7</sub> I, -20°, 4 hr C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br, -20°, 4 hr	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (67) A, R = C <sub>3</sub> H <sub>7</sub> - <i>n</i> (-) A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (trace) A, R = C <sub>3</sub> H <sub>7</sub> - <i>n</i> (51) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (64)	432 432 432 432
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -20°, 10 min	NH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> Br	A, CH <sub>2</sub> =C=C(C <sub>2</sub> H <sub>5</sub> )OCH <sub>3</sub> + B, C <sub>2</sub> H <sub>5</sub> CH=C=CHOCH <sub>3</sub> + C, C <sub>2</sub> H <sub>5</sub> C≡CCH <sub>2</sub> OCH <sub>3</sub> A: 45, B: 45, C: 10 (55)	432
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -40°, 10 min	CH <sub>3</sub> COCH <sub>2</sub> Br, -30°, 45 min, then KOH, ether, 0°	CH <sub>2</sub> =C=CROCH <sub>3</sub> A, R =  (50-75)	562
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -40°, 10 min	CH <sub>3</sub> COCH(CH <sub>3</sub> )Br, -30°, 45 min, then KOH, ether, 0°	A, R =  (50-75)	562
			CH <sub>3</sub> COC(CH <sub>3</sub> ) <sub>2</sub> Br, -30°, 45 min, then KOH, ether, 0°	A, R =  (50-75)	562
		C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> Br, -30°, 45 min, then KOH, ether, 0°	A, R =  (50-75)	562	
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> COCH <sub>2</sub> Br, -30°, 45 min, then KOH, ether, 0°	A, R =  (50-75)	562	
		NaNH <sub>2</sub> , NH <sub>3</sub> , ether	C <sub>2</sub> H <sub>5</sub> Br	A, CH <sub>2</sub> =C=CROCH <sub>3</sub> + B, RCH=C=CHOCH <sub>3</sub> A: 63, B: 37, R = C <sub>2</sub> H <sub>5</sub> (35) A: 54, B: 46, R = C <sub>3</sub> H <sub>7</sub> - <i>n</i> (41) A: 53, B: 47, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (44) A: 55, B: 45, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (45) A: 56, B: 44, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (45)	432 432 432 432
		NH <sub>3</sub> , ether, NaNH <sub>2</sub> , LiNH <sub>2</sub> , KNH <sub>2</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br <i>n</i> -C <sub>4</sub> H <sub>9</sub> Br		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA, -65°, then -27°, 2 hr	(CH <sub>3</sub> CO) <sub>2</sub> O (CH <sub>3</sub> ) <sub>3</sub> SiCl	CH <sub>2</sub> =CHCH=CHOCOCH <sub>3</sub> (65) <i>cis</i> CH <sub>2</sub> =CHCH=CHOSi(CH <sub>3</sub> ) <sub>3</sub> (69) <i>cis</i>	215 215
CH <sub>2</sub> =CHCH <sub>2</sub> OCH <sub>3</sub>		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -65°, 10 min	 A, RCH <sub>2</sub> CH=CHOCH <sub>3</sub> + B, CH <sub>2</sub> =CHCHROCH <sub>3</sub> A: 72, B: 28, R =  (93) A: 68, B: 32, R = CH(OH)CH(CH <sub>3</sub> ) <sub>2</sub> (99)	127 127	
	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, ZnCl <sub>2</sub> (1 eq), -65°, 10 min	 A: 0, B: 1, R =  (92)	127		
C <sub>5</sub>	CH <sub>3</sub> C≡CCH <sub>2</sub> OCH <sub>3</sub> HC≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	NaNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq) <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), neat, 70°, 2-3 hr	H <sub>2</sub> O -	HC≡CCH=CH <sub>2</sub> (82) CH <sub>2</sub> =C=CHOC <sub>2</sub> H <sub>5</sub> (85)	183 432
	CH <sub>2</sub> =C=CHOC <sub>2</sub> H <sub>5</sub>	NaNH <sub>2</sub> , NH <sub>3</sub> , ether	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br	A, CH <sub>2</sub> =C=CROC <sub>2</sub> H <sub>5</sub> + B, RCH=C=CHOC <sub>2</sub> H <sub>5</sub> A: 50, B: 50, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (5) A: 63, B: 37, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (48)	432 432
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br		



TABLE X. ETHERS (Continued)



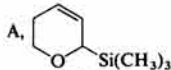
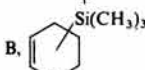
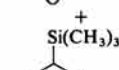
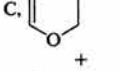
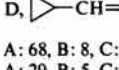
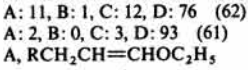
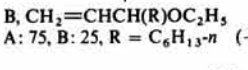

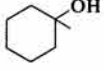

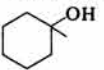

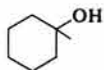
No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>5</sub> (Contd.) 	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -65°, then -27°, 17 hr	(CH <sub>3</sub> CO) <sub>2</sub> O	 (8)	215	
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, TMEDA, -65°, then -27°, 1 hr	(CH <sub>3</sub> ) <sub>3</sub> SiCl	A,  +  B,  +  C,  +  (66) D,  (67)	215 215 215 215	
CH <sub>2</sub> =CHCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	-27°, 1 hr -27°, 16 hr -27°, 64 hr -27°, 260 hr	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I	A, RCH <sub>2</sub> CH=CHOC <sub>2</sub> H <sub>5</sub> + B, CH <sub>2</sub> =CHCH(R)OC <sub>2</sub> H <sub>5</sub>	215 215 215 215	
	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -65°, 10 min		A, RCH <sub>2</sub> CH=CHOC <sub>2</sub> H <sub>5</sub> + B, CH <sub>2</sub> =CHCH(R)OC <sub>2</sub> H <sub>5</sub>	A: 75, B: 25, R = C <sub>6</sub> H <sub>13</sub> - <i>n</i> (-)	127
			A: 75, B: 25, R =  (-)	127	
C <sub>6</sub>	HC≡CCH <sub>2</sub> OCH <sub>2</sub> C≡CH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA, -80°	H <sub>2</sub> O	HC≡CCH(OH)CH=C=CH <sub>2</sub> (10)	440
	CH <sub>2</sub> =CHCH <sub>2</sub> OCH <sub>2</sub> CH=CH <sub>2</sub>	KNH <sub>2</sub> (2 eq), NH <sub>3</sub> , ether	-	CH <sub>2</sub> =CHCH(OH)CH <sub>2</sub> CH=CH <sub>2</sub> (40)	208
	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -65°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I	A, RCH <sub>2</sub> C(CH <sub>3</sub> )=CHOC <sub>2</sub> H <sub>5</sub> + B, CH <sub>2</sub> =C(CH <sub>3</sub> )CHROC <sub>2</sub> H <sub>5</sub>	127 127
			(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Br CH <sub>3</sub> SSCH <sub>3</sub>	A: 63, B: 37, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (41) A: 90, B: 10, R = SCH <sub>3</sub> (79)	127 127
				A: 50, B: 50, R =  (93)	127
		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -65°, ZnCl <sub>2</sub> (1 eq)		A: 0, B: 97, R = 	127
	CH <sub>2</sub> =CHCH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO	(CH <sub>3</sub> ) <sub>3</sub> SiCl	CH <sub>2</sub> =CHCH[Si(CH <sub>3</sub> ) <sub>3</sub> ]OR	240a
			(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiCl	A, R = (CH <sub>3</sub> ) <sub>3</sub> Si (80)	240a
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> (CH <sub>3</sub> ) <sub>2</sub> SiCl	A, R = (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Si (72)	240a
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> (CH <sub>3</sub> ) <sub>2</sub> SiCl	A, R = <i>t</i> -C <sub>4</sub> H <sub>9</sub> (CH <sub>3</sub> ) <sub>2</sub> Si (76)	240a
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 1.5 hr	(CH <sub>3</sub> ) <sub>3</sub> SiCl, -78°, 30 min	A, CH <sub>2</sub> =CHCH(R)OSi(CH <sub>3</sub> ) <sub>3</sub> + B, CH <sub>2</sub> (R)CH=CHOSi(CH <sub>3</sub> ) <sub>3</sub>	240b 240b
			(CH <sub>3</sub> ) <sub>3</sub> SiF, -78°, 30 min	A: 100, B: 0, R = (CH <sub>3</sub> ) <sub>3</sub> Si (75) A: 100, B: 0, R = (CH <sub>3</sub> ) <sub>3</sub> Si (50)	240b 240b
			(CH <sub>3</sub> ) <sub>3</sub> SiBr, -78°, 30 min	A: 100, B: 0, R = (CH <sub>3</sub> ) <sub>3</sub> Si (50)	240b
			(CH <sub>3</sub> ) <sub>3</sub> SiI, -78°, 30 min	A: 100, B: 0, R = (CH <sub>3</sub> ) <sub>3</sub> Si (50)	240b
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (1.2%)	(CH <sub>3</sub> ) <sub>3</sub> SiF, -78°, 30 min	A: 35, B: 65, R = (CH <sub>3</sub> ) <sub>3</sub> Si (-)	240b
			ZnCl <sub>2</sub> added (CH <sub>3</sub> ) <sub>3</sub> SiCl, -78°, 30 min	A: 100, B: 0, R = (CH <sub>3</sub> ) <sub>3</sub> Si (45) A: 50, B: 50, R = (CH <sub>3</sub> ) <sub>3</sub> Si (75)	240b 240b
		ZnCl <sub>2</sub> added (CH <sub>3</sub> ) <sub>3</sub> SiBr, -78°, 30 min	A: 100, B: 0, R = (CH <sub>3</sub> ) <sub>3</sub> Si (68) A: 75, B: 25, R = (CH <sub>3</sub> ) <sub>3</sub> Si (70)	240b 240b	
		ZnCl <sub>2</sub> added (CH <sub>3</sub> ) <sub>3</sub> SiI, -78°, 30 min	A: 100, B: 0, R = (CH <sub>3</sub> ) <sub>3</sub> Si (40) A: 85, B: 15, R = (CH <sub>3</sub> ) <sub>3</sub> Si (50)	240b 240b	

TABLE X. ETHERS (Continued)



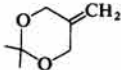
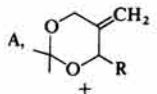
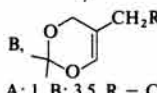





No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.		
C <sub>6</sub> (Contd.)	CH <sub>2</sub> =CHCH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiCl, -78°, 30 min	CH <sub>2</sub> =CHCH[Si(CH <sub>3</sub> ) <sub>3</sub> ]OSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (75)	240b		
			ClCO <sub>2</sub> CH <sub>3</sub> , -78°, 30 min	CH <sub>2</sub> =CHCH(R)Si(CH <sub>3</sub> ) <sub>3</sub> A, R = OCO <sub>2</sub> CH <sub>3</sub> (68)	240b		
			ClCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , -78°, 30 min	A, R = OCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (74)	240b		
			C <sub>6</sub> H <sub>5</sub> OCO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> , -78°, 30 min	A, R = OCO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (45)	240b		
			CH <sub>3</sub> OCO <sub>2</sub> CH <sub>3</sub> , -78°, 30 min	A, CH <sub>2</sub> =CHCH[Si(CH <sub>3</sub> ) <sub>3</sub> ]OCO <sub>2</sub> CH <sub>3</sub> + B, CH <sub>3</sub> OCOCH <sub>2</sub> CH=CHOSi(CH <sub>3</sub> ) <sub>3</sub> A: 32, B: 67 (43)	240b		
			C <sub>2</sub> H <sub>5</sub> OCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , -78°, 30 min	A, CH <sub>2</sub> =CHCH[Si(CH <sub>3</sub> ) <sub>3</sub> ]OCOC <sub>2</sub> H <sub>5</sub> + B, C <sub>2</sub> H <sub>5</sub> OCOCH <sub>2</sub> CH=CHOSi(CH <sub>3</sub> ) <sub>3</sub> A: 45, B: 35 (43)	240b		
			C <sub>2</sub> H <sub>5</sub> Br	(CH <sub>3</sub> ) <sub>2</sub> C=C=C=CROCH <sub>3</sub> A, R = C <sub>2</sub> H <sub>5</sub> (80) A, R = CH <sub>2</sub> OH (55)	576 576		
			CH <sub>2</sub> O, -30°, then reflux, 30 min	A, R = CH(OH)CH <sub>3</sub> (74)	576		
			CH <sub>3</sub> CHO, -30°	A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (71)	576		
			CH <sub>3</sub> COCH <sub>3</sub> , -30°	A, R = C(OH)(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (68)	576		
C <sub>7</sub>	(CH <sub>3</sub> ) <sub>2</sub> C=C=C=CHOCH <sub>3</sub>	LiNH <sub>2</sub> , NH <sub>3</sub> (liq)	C <sub>2</sub> H <sub>5</sub> Br	(CH <sub>3</sub> ) <sub>2</sub> C=C=C=CROCH <sub>3</sub> A, R = C <sub>2</sub> H <sub>5</sub> (80) A, R = CH <sub>2</sub> OH (55)	576 576		
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -30°, -25°, 10 min	CH <sub>2</sub> O, -30°, then reflux, 30 min	A, R = CH(OH)CH <sub>3</sub> (74)	576	
				CH <sub>3</sub> CHO, -30°	A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (71)	576	
				C <sub>2</sub> H <sub>5</sub> COC <sub>2</sub> H <sub>5</sub> , -30°	A, R = C(OH)(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (68)	576	
				 , -30°	A, R =  (90)	576	
			CH <sub>2</sub> =C(CH <sub>3</sub> )CH=C=CHOCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -30°, -25°, 10 min	CH <sub>3</sub> COCH <sub>3</sub> , -30°	CH <sub>2</sub> =C(CH <sub>3</sub> )CH=C=C(OCH <sub>3</sub> )C(OH)(CH <sub>3</sub> ) <sub>2</sub> (-)	576
			CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> OCH=CHCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>14</sub> , ether, TMEDA, 5°, then 25°, 16 hr	H <sub>2</sub> O	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(OH)CH=CHCH <sub>3</sub> (80)	202
			<i>cis</i> -CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> OCH=CHCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>14</sub> , ether, TMEDA, 5°, then 25°, 16 hr	H <sub>2</sub> O	<i>cis</i> -CH <sub>2</sub> =C(CH <sub>3</sub> )CH(OH)CH=CHCH <sub>3</sub> (34)	202
			<i>trans</i> -CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> OCH=CHCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>14</sub> , ether, TMEDA, 5°, then 25°, 16 hr	H <sub>2</sub> O	<i>trans</i> -CH <sub>2</sub> =C(CH <sub>3</sub> )CH(OH)CH=CHCH <sub>3</sub> (34)	202
			122		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	CH <sub>3</sub> I	A,  + B, 
CH <sub>2</sub> =CHCH <sub>2</sub> Br	A: 1, B: 3.5, R = CH <sub>3</sub> (98)	618					
(CH <sub>3</sub> ) <sub>2</sub> (C <sub>4</sub> H <sub>9</sub> - <i>t</i> )SiCl	A: 1, B: 1.5, R = CH <sub>2</sub> =CHCH <sub>2</sub> (100)	618					
CH <sub>3</sub> CHCH <sub>3</sub>	A: 1, B: 19, R = (CH <sub>3</sub> ) <sub>2</sub> (C <sub>4</sub> H <sub>9</sub> - <i>t</i> )Si (99)	618					
	A: 1, B: 2.8, R = CH(CH <sub>3</sub> )CH(OH)CH <sub>3</sub> (39)	618					
<i>cis</i> - 	A: 7.5, B: 1, R =  (95)	618					
C <sub>6</sub> H <sub>5</sub> CHO, THF	A: 1.2, B: 1, R = C <sub>6</sub> H <sub>5</sub> CH(OH) (85)	618					
[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, THF	A: 1, B: 4 (95)	618					
THF, CdCl <sub>2</sub>	A: 3.4, B: 1 (95)	618					
THF, ZnCl <sub>2</sub>	A: 19, B: 1 (100)	618					
123	CH <sub>2</sub> =CHCH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> - <i>n</i>	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Li (1.3 eq), C <sub>5</sub> H <sub>12</sub> , TMEDA, 25°, 30 min	Hydrolysis	<i>n</i> -C <sub>6</sub> H <sub>13</sub> CHO (30)	203		
			<i>n</i> -C <sub>3</sub> H <sub>7</sub> Li, THF-C <sub>5</sub> H <sub>12</sub> , 1:1	Hydrolysis	CH <sub>2</sub> =CHCH(OH)C <sub>4</sub> H <sub>9</sub> - <i>n</i> (-) + <i>n</i> -C <sub>6</sub> H <sub>13</sub> CHO (29)	203	
			<i>n</i> -C <sub>3</sub> H <sub>7</sub> Li, C <sub>5</sub> H <sub>12</sub>		CH <sub>2</sub> =CHCH(OH)C <sub>4</sub> H <sub>9</sub> - <i>n</i> (23)	203	
			<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -65°, 10 min	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I	CH <sub>2</sub> =CHC <sub>4</sub> H <sub>9</sub> - <i>n</i> (73) A, RCH <sub>2</sub> CH=CHOC <sub>4</sub> H <sub>9</sub> - <i>t</i> (83) + B, CH <sub>2</sub> =CHCH(R)OC <sub>4</sub> H <sub>9</sub> - <i>t</i> A: 89, B: 11, R = C <sub>6</sub> H <sub>13</sub> - <i>n</i> (93)	127 127 127	
				Br(CH <sub>2</sub> ) <sub>4</sub> Br	A: 80, B: 20, R = (CH <sub>2</sub> ) <sub>4</sub> Br (90)	127	
				<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	A: 64, B: 36, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (65)	127	
				CH <sub>3</sub> SSCH <sub>3</sub>	A: 95, B: 5, R = SCH <sub>3</sub> (-)	127	
					A: 23, B: 73, R =  (72)	127	

TABLE X. ETHERS (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF-ether, 2.6:1, -74°, 60 min	D <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CHDOCH <sub>3</sub> (0.95 D) (-)	174
			H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>3</sub> (52) + C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> (1) + C <sub>6</sub> H <sub>5</sub> CHO (0.3) + polymers (45)	174
	CH <sub>3</sub> C≡CCH <sub>2</sub> OCH <sub>2</sub> C≡CCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA, -80°	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>3</sub> (35) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>3</sub> (15) + polymers (32)	173
			H <sub>2</sub> O	CH <sub>3</sub> C≡CCH(OH)C(CH <sub>3</sub> )=C=CH <sub>2</sub> (64)	440
	<i>i</i> -C <sub>3</sub> H <sub>7</sub> C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> <i>n</i> -C <sub>4</sub> H <sub>9</sub> C≡COC <sub>2</sub> H <sub>5</sub> CH <sub>3</sub> C≡CCH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> - <i>n</i> C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA, -80°	H <sub>2</sub> O	HC≡CCH=C(CH <sub>3</sub> ) <sub>2</sub> (85)	183
			H <sub>2</sub> O	HC≡CCH=CHC <sub>2</sub> H <sub>5</sub> (42)	183
			H <sub>2</sub> O	HC≡CCH=CH <sub>2</sub> (82)	183
			H <sub>2</sub> O	HC≡CCH=CHOC <sub>2</sub> H <sub>5</sub> (79)	183
			H <sub>2</sub> O	CH <sub>2</sub> =C=C=CHOC <sub>2</sub> H <sub>5</sub> (72)	170
	CH <sub>2</sub> =CHCH <sub>2</sub> OTHP	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -65°, 10 min	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I	A, <i>n</i> -C <sub>7</sub> H <sub>15</sub> CH=CHOTHP	170
B, CH <sub>2</sub> =CHCH(C <sub>6</sub> H <sub>13</sub> - <i>n</i> )OTHP A: 54, B: 46 (-)				127	
CH <sub>3</sub> CH=CHOTHP	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq), <i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), THF, -78°, 1 hr	CH <sub>3</sub> I	CH <sub>3</sub> CH=C(CH <sub>3</sub> )OTHP (83) + C <sub>2</sub> H <sub>5</sub> CH=CHOTHP (4) + CH <sub>2</sub> =CHCH(CH <sub>3</sub> )OTHP (<0.5) + CH <sub>3</sub> CH=CHOTHP (7)	105	
			Hydrolysis	<i>n</i> -C <sub>4</sub> H <sub>9</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CHO (-)	203
			C <sub>6</sub> H <sub>5</sub> CHO	(CH <sub>3</sub> ) <sub>3</sub> SiC≡CCHROC <sub>2</sub> H <sub>5</sub> A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (80) A, R = CH(OH)C <sub>7</sub> H <sub>15</sub> - <i>n</i> (72) A, R = CH(OH)C≡CC <sub>5</sub> H <sub>11</sub> - <i>n</i> (80)	30 30 30
C <sub>9</sub>	CH≡CCH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CH=CH <sub>2</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK NaNH <sub>2</sub> , CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , room temperature, 3 hr KNH <sub>2</sub> , NH <sub>3</sub> (liq), 2 hr	-	CH <sub>2</sub> =C=CHOC <sub>6</sub> H <sub>5</sub> (67.5)	538
			H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> OCH=CHCH <sub>3</sub> <i>cis</i> : 97, <i>trans</i> : 3 (-)	395
	CH <sub>3</sub> CH=CHCH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> - <i>n</i> (CH <sub>3</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Li, C <sub>6</sub> H <sub>12</sub> , THF <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 1 hr, ZnI <sub>2</sub> , THF, -70°, 1 hr	Hydrolysis C <sub>6</sub> H <sub>5</sub> CHO	<i>n</i> -C <sub>7</sub> H <sub>15</sub> CHO	30
				<i>n</i> -C <sub>5</sub> H <sub>11</sub> C≡CCHO	30
	CH <sub>3</sub> CH=CHCH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub>	NaNH <sub>2</sub> , THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 40°, 10 hr	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> OH (68) + C <sub>6</sub> H <sub>5</sub> OCH=CHCH <sub>3</sub> <i>cis</i> : 65, <i>trans</i> : 35 (32)	395
				CH <sub>3</sub> CH=CHOC <sub>6</sub> H <sub>5</sub> <i>cis</i> : 84, <i>trans</i> : 16 (56)	601
	CH <sub>3</sub> CH=CHCH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> - <i>n</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 40°, 5 min	H <sub>2</sub> O	<i>cis</i> : 94, <i>trans</i> : 6 (67)	601
				H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> COC <sub>2</sub> H <sub>5</sub> (53)
	CH <sub>3</sub> CH=CHCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , room temperature, 4 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , 0°, 90 sec	CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> CH(OCH <sub>3</sub> )CH=CH <sub>2</sub> (58) + C <sub>6</sub> H <sub>5</sub> OCH=CHC <sub>2</sub> H <sub>5</sub> (18) <i>cis</i> + C <sub>6</sub> H <sub>5</sub> COC <sub>3</sub> H <sub>7</sub> - <i>i</i> (21) + C <sub>6</sub> H <sub>5</sub> COC <sub>4</sub> H <sub>9</sub> - <i>t</i> (4) + C <sub>6</sub> H <sub>5</sub> COCH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub> (0.5)	395

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TABLE X. ETHERS (Continued)




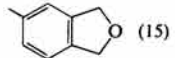
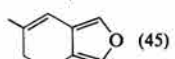
No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>9</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CH=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , room temperature, 30 min	H <sub>2</sub> O C <sub>6</sub> H <sub>5</sub> COC <sub>2</sub> H <sub>5</sub> (40) + C <sub>6</sub> H <sub>5</sub> CH(OH)CH=CH <sub>2</sub> (30) + C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CH=CH <sub>2</sub> (20)	395
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	CH <sub>3</sub> I A, C <sub>6</sub> H <sub>5</sub> OCH=CHC <sub>2</sub> H <sub>5</sub> <i>cis</i> + B, C <sub>6</sub> H <sub>5</sub> OCH(CH <sub>3</sub> )CH=CH <sub>2</sub> A: 71, B: 24 (-)	32
		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -65°, 10 min	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I A, <i>n</i> -C <sub>7</sub> H <sub>13</sub> CH=CHOC <sub>6</sub> H <sub>5</sub> + B, CH <sub>2</sub> =CHCH(C <sub>6</sub> H <sub>13</sub> - <i>n</i> )OC <sub>6</sub> H <sub>5</sub> A: 63, B: 37 (-)	127
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li- <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq each), petroleum ether, -30°, 1 hr	 CH <sub>3</sub> I, -30° A,  + B,  A: 24, B: 76 (-) A, C <sub>2</sub> H <sub>5</sub> CH=CHOC <sub>6</sub> H <sub>5</sub> (Z) + B, CH <sub>2</sub> =CHCH(CH <sub>3</sub> )OC <sub>6</sub> H <sub>5</sub> + C, <i>n</i> -C <sub>5</sub> H <sub>11</sub> CH=CHOC <sub>6</sub> H <sub>5</sub> (Z) + D, CH <sub>2</sub> =CHCH(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )OC <sub>6</sub> H <sub>5</sub> + E, CH <sub>2</sub> =CHCH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub> A (44), B (16), C (13), D (2), E (7)	127
	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80°, 1 hr	CH <sub>3</sub> I A, C <sub>2</sub> H <sub>5</sub> CH=CHOC <sub>6</sub> H <sub>5</sub> (Z) + B, CH <sub>2</sub> =CHCH(CH <sub>3</sub> )OC <sub>6</sub> H <sub>5</sub> + C, CH <sub>2</sub> =CHCH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub> + D, CH <sub>2</sub> =CHCH <sub>2</sub> OH A (47), B (12), C (11), D (3)	89	
	CH <sub>3</sub> CH=CHOC <sub>6</sub> H <sub>5</sub> (Z)	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li- <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq each), petroleum ether, 25°, 1 hr	CH <sub>3</sub> I, 0°, 1 hr A, C <sub>2</sub> H <sub>5</sub> CH=CHOC <sub>6</sub> H <sub>5</sub> (Z) + B, CH <sub>3</sub> CH=CHOC <sub>6</sub> H <sub>5</sub> (Z) + C, CH <sub>2</sub> =CHCH(CH <sub>3</sub> )OC <sub>6</sub> H <sub>5</sub> A (49), B (4), C (1)	89
	C <sub>6</sub> H <sub>5</sub> OCD <sub>2</sub> CH=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , room temperature, 4 hr	H <sub>2</sub> O C <sub>6</sub> H <sub>5</sub> OH (-) + C <sub>6</sub> H <sub>5</sub> OCD <sub>2</sub> CH=CH <sub>2</sub> (-) + C <sub>6</sub> H <sub>5</sub> CD(OH)CH=CH <sub>2</sub> (-)	395
	CH <sub>2</sub> =C(CH <sub>3</sub> )C≡CCH <sub>2</sub> OCH <sub>2</sub> C≡CH	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, room temperature, 4 days	-  (15) +  (45)	342
	CH <sub>3</sub> C≡CCH(CH <sub>3</sub> )OCH <sub>2</sub> C≡CCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA, -80°	H <sub>2</sub> O CH <sub>3</sub> C≡CCH(OH)C(CH <sub>3</sub> )=C=CHCH <sub>3</sub> (9) + CH <sub>3</sub> C≡CCH(OH)CH(CH <sub>3</sub> )C≡CCH <sub>3</sub> (31)	440
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF-ether, 2.6:1, -60°	H <sub>2</sub> O C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>2</sub> H <sub>5</sub> (34) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH (33) + polymers (10)	174
			D <sub>2</sub> O C <sub>6</sub> H <sub>5</sub> CHDOC <sub>2</sub> H <sub>5</sub> (-) (0.85D)	174

TABLE X. ETHERS (Continued)

No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>9</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> Li (1 eq), ether, room temperature, 40 hr	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> (34) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH (44) + polymers (15)	173
	C <sub>6</sub> H <sub>5</sub> CD <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Na, <i>n</i> -C <sub>8</sub> H <sub>18</sub> , 0° to 48°	C <sub>6</sub> H <sub>5</sub> CHDOH (-) + C <sub>2</sub> H <sub>4</sub> (-)	176
		<i>n</i> -C <sub>3</sub> H <sub>7</sub> Na	C <sub>6</sub> H <sub>5</sub> CHDOH (-) + C <sub>2</sub> H <sub>4</sub> (91) + <i>n</i> -C <sub>3</sub> H <sub>7</sub> D (81) + <i>n</i> -C <sub>3</sub> H <sub>8</sub> (31)	175
	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C=C=C=CHOCH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , 25°, 30 min	CH <sub>2</sub> =CHC(C <sub>2</sub> H <sub>5</sub> )=CHCH=CHOCH <sub>3</sub> <i>cis</i> : 1, <i>trans</i> : 1 (76)	576
		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li (1.25eq), THF, -78°	A,  + B,  A: 1, B: 2 (-)	190
		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li (1.25 eq), THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 96:4, -78°	(86)	190
		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li (excess), THF, -78°	(-)	190
	HC≡CCH <sub>2</sub> OC <sub>6</sub> H <sub>13-n</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), neat, 70°, 2-3 hr	CH <sub>2</sub> =C=CHOC <sub>6</sub> H <sub>13-n</sub> (92)	432
	C <sub>2</sub> H <sub>5</sub> OCH(CH <sub>3</sub> )C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	KNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq) <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -40° to -50°, 35 min	HC≡CCH=CHCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> (75) CH <sub>3</sub> CH=C=C=CHOC <sub>2</sub> H <sub>5</sub> <i>cis</i> : 1, <i>trans</i> : 1 (76)	183 170
	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiOCH <sub>2</sub> CH=CH <sub>2</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	A, (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiOCH=CHCH <sub>2</sub> R <i>cis</i> + B, (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiOCHRCH=CH <sub>2</sub> A: 97, B: 3, R = CH <sub>3</sub> (>95) A: 83, B: 17, R = C <sub>2</sub> H <sub>5</sub> (>95) A: 84, B: 16, R = C <sub>3</sub> H <sub>7-n</sub> (>95) A: 60, B: 40, R = C <sub>3</sub> H <sub>7-i</sub> (>95)	32 32 32
		<i>n</i> -C <sub>3</sub> H <sub>7</sub> I <i>i</i> -C <sub>3</sub> H <sub>7</sub> I	A: 39, B: 61, R =  (80)	32
		<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br CH <sub>2</sub> =CHCH <sub>2</sub> Br (CH <sub>3</sub> ) <sub>3</sub> SiCl, -78°, 30 min	A: 75, B: 25, R = C <sub>3</sub> H <sub>7-n</sub> (>95) A: 68, B: 32, R = CH <sub>2</sub> CH=CH <sub>2</sub> (>95) CH <sub>2</sub> =CHCHSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> (85)	32 32 240b
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 1.5 hr [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 1.2% added [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 1.2% added	ZnCl <sub>2</sub> added (CH <sub>3</sub> ) <sub>3</sub> SiCl, -78°, 30 min	240b 240b
		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF: [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO	B, (CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> CH=CHOSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> A, 50, B: 50 (87) CH <sub>2</sub> =CHCHSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> OR A, R=(CH <sub>3</sub> ) <sub>3</sub> Si (60) A, R = (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Si (71)	240a 240a
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> (CH <sub>3</sub> ) <sub>2</sub> SiOCH <sub>2</sub> CH=CH <sub>2</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	A, <i>n</i> -C <sub>4</sub> H <sub>9</sub> (CH <sub>3</sub> ) <sub>2</sub> SiOCH=CHC <sub>4</sub> H <sub>9-n</sub> <i>cis</i> + B, <i>n</i> -C <sub>4</sub> H <sub>9</sub> (CH <sub>3</sub> ) <sub>2</sub> SiOCH(C <sub>3</sub> H <sub>7-n</sub> )CH=CH <sub>2</sub> A: 81, B: 19 (>95)	32

TABLE X. ETHERS (Continued)

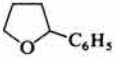
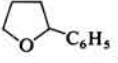
No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>10</sub> C <sub>6</sub> H <sub>5</sub> C≡CCH <sub>2</sub> OCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -75°, 15 min, or THF, -75°, then -50°	(CH <sub>3</sub> ) <sub>3</sub> SiCl (2 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO  (CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> (2 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO CH <sub>3</sub> I (2 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, (CH <sub>3</sub> ) <sub>3</sub> SiCl (1 eq), then CH <sub>3</sub> I (1 eq) [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, CH <sub>3</sub> I (1 eq), then (CH <sub>3</sub> ) <sub>3</sub> SiCl [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, C <sub>2</sub> H <sub>5</sub> Br (1 eq), then (CH <sub>3</sub> ) <sub>3</sub> SiCl (1 eq) [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, C <sub>2</sub> H <sub>5</sub> Br (1 eq), then CH <sub>3</sub> I (1 eq) [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, (CH <sub>3</sub> ) <sub>3</sub> SiCl (1 eq), then (CH <sub>3</sub> ) <sub>2</sub> CO (1 eq) [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, (CH <sub>3</sub> ) <sub>3</sub> SiCl (1 eq), then CO <sub>2</sub> [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, C <sub>2</sub> H <sub>5</sub> Br (1 eq), then H <sub>2</sub> O [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, <i>n</i> -C <sub>4</sub> H <sub>9</sub> Br (1 eq), then H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> (R)C=C=CR'OCH <sub>3</sub> A, R = R' = Si(CH <sub>3</sub> ) <sub>3</sub> (80)  A, R = R' = CH <sub>3</sub> (70)  A, R = R' = CH <sub>3</sub> (70)  A, R = Si(CH <sub>3</sub> ) <sub>3</sub> , R' = CH <sub>3</sub> (70)  A, R = CH <sub>3</sub> , R' = Si(CH <sub>3</sub> ) <sub>3</sub> (78)  A, R = C <sub>2</sub> H <sub>5</sub> , R' = Si(CH <sub>3</sub> ) <sub>3</sub> (82)  A, R = C <sub>2</sub> H <sub>5</sub> , R' = CH <sub>3</sub> (76)  A, R = Si(CH <sub>3</sub> ) <sub>3</sub> , R' = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (80)  A, R = Si(CH <sub>3</sub> ) <sub>3</sub> , R' = CO <sub>2</sub> H (90)  A, R = C <sub>2</sub> H <sub>5</sub> , R' = H (-)  A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> , R' = H (-)	124, 125  124, 125 124 124, 125 124 124, 125 124 124, 125 124 124, 125 124 124, 125 124
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> CH=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 1 hr, ZnI <sub>2</sub> , THF, -70°, 1 hr  <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -65°, 10 min  <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , room temperature, 4 hr  <i>n</i> -C <sub>3</sub> H <sub>7</sub> Na	C <sub>6</sub> H <sub>5</sub> CHO  <i>n</i> -C <sub>5</sub> H <sub>11</sub> C≡CCHO [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, C <sub>2</sub> H <sub>5</sub> I, -65°  H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> C≡CCHROCH <sub>3</sub> A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (78) A, R = CH(OH)C≡CC <sub>5</sub> H <sub>11</sub> - <i>n</i> (61) C <sub>6</sub> H <sub>5</sub> C(C <sub>2</sub> H <sub>5</sub> )=C=CHOCH <sub>3</sub> (60)  <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COC <sub>2</sub> H <sub>5</sub> (62)	30 30 274 203
	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Li <i>n</i> -C <sub>3</sub> H <sub>7</sub> Na, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , -60° to 0°	H <sub>2</sub> O —	C <sub>2</sub> H <sub>4</sub> (95) + <i>n</i> -C <sub>3</sub> H <sub>8</sub> (98) + C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>3</sub> (3) + C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )(OH)CH(OH)C <sub>6</sub> H <sub>5</sub> (26) C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> (85-92) C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> (57) + C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>3</sub> (3) +  (6) + C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )(OH)C(CH <sub>3</sub> )(OH)C <sub>6</sub> H <sub>5</sub> (26) + CH <sub>2</sub> =CH <sub>2</sub> (99) C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> (85-92)	105 176  176 176
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> CH=CH <sub>2</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, CH <sub>3</sub> SOCH <sub>3</sub> , 37°, 3 days	—	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH=CHCH <sub>3</sub> (84)	202
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH=CHCH <sub>3</sub> <i>trans</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>14</sub> , ether, TMEDA, -65°, then -27°, 16 hr	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH(OH)CH=CHCH <sub>3</sub> (100) <i>trans</i>	202

TABLE X. ETHERS (Continued)

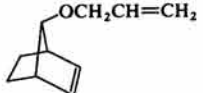
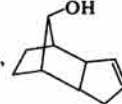
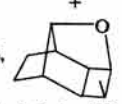
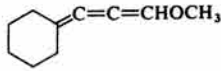
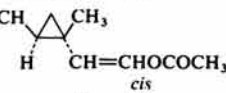
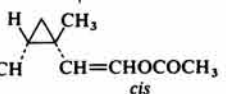
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>10</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH=CHCH <sub>3</sub> <i>cis</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>14</sub> , ether, TMEDA, -65°, then -27°, 16 hr	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH(OH)CH=CHCH <sub>3</sub> (87) <i>cis</i>	202
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>14</sub> , ether, TMEDA, -65°, then -27°, 5 hr	D <sub>2</sub> O, -75°	A, C <sub>6</sub> H <sub>5</sub> CHDOCH=CHCH <sub>3</sub> (0.8 D) <i>cis</i> + B, C <sub>6</sub> H <sub>5</sub> CH(OH)CH=CHCH <sub>3</sub> <i>cis</i> A: 1, B: 3 (95)	202
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>14</sub> , ether, TMEDA, -65°, then -27°, 4 hr	(CH <sub>3</sub> ) <sub>3</sub> SiCl	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH=CHCH <sub>3</sub> (-) <i>cis</i> + C <sub>6</sub> H <sub>5</sub> CH[Si(CH <sub>3</sub> ) <sub>3</sub> ]OCH=CHCH <sub>3</sub> (-) <i>cis</i> + C <sub>6</sub> H <sub>5</sub> CH[OSi(CH <sub>3</sub> ) <sub>3</sub> ]CH=CHCH <sub>3</sub> (-) <i>cis</i>	202
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OC <sub>3</sub> H <sub>7-i</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -40°, 30 min	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>3</sub> H <sub>7-i</sub> (73) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH (22) + C <sub>6</sub> H <sub>5</sub> COC <sub>3</sub> H <sub>7-i</sub> (-) + <i>i</i> -C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>4</sub> CHO- <i>p</i> (-) + C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>3</sub> H <sub>7-i</sub> (62)	198
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF-ether, 2.6:1, -60°, 10 min	H <sub>2</sub> O, 25°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH (13) + C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>4</sub> H <sub>9-n</sub> (7) + polymers (7)	174
			D <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CHDOC <sub>3</sub> H <sub>7-i</sub> (-) (0.86 D)	174
		CH <sub>3</sub> Li (excess), THF-ether, 1:1, room temperature	H <sub>2</sub> O	A,  + B,  A: 3, B: 7 (55)	189
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , 20°, 1 min	-	CH=C=CHOCH <sub>3</sub> (-)	576
		40°, 20 min	-	CHCH=CHOCH <sub>3</sub> (79) <i>cis</i> : 1, <i>trans</i> : 1	576
		60°, 70°, 1 hr	-	C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>3</sub> (82) <i>trans</i>	576
	HC≡CCH <sub>2</sub> OCH <sub>2</sub> C≡CC <sub>4</sub> H <sub>9-n</sub>	NaNH <sub>2</sub> (3 eq), NH <sub>3</sub> (liq) <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, TMEDA, -65°, then -27°, 28 hr	H <sub>2</sub> O (CH <sub>3</sub> CO) <sub>2</sub> O	HC≡CCH=CHC <sub>3</sub> H <sub>7-n</sub> (61)  <i>cis</i> +  <i>cis</i> (62)	183 215

TABLE X. ETHERS (Continued)

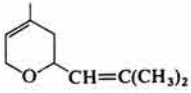
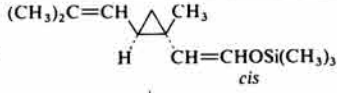
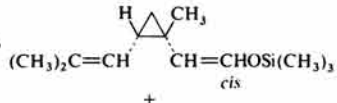
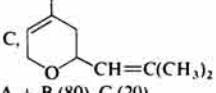
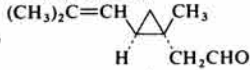
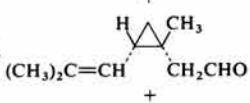
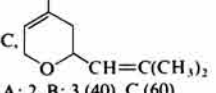
No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>10</sub> (Contd.) 	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, TMEDA, -65°	(CH <sub>3</sub> ) <sub>3</sub> SiCl	A,  + B,  + C, 		
	-27°, 10 min -27°, 2.5 hr		A + B (80), C (20) A + B (79), C (trace)	215 215	
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, TMEDA, -65°	H <sub>2</sub> O	A,  + B,  + C, 	A: 2, B: 3 (40), C (60)	215
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, TMEDA, -65°, then -27°, 10 min			A: 3, B: 2.9 (40), C (0)	215
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C=C=C=CHOC <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -5°, 1.5 hr	CH <sub>3</sub> COCH <sub>3</sub> , -20°, 30 min	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C=C=C(OC <sub>2</sub> H <sub>5</sub> )C(OH)(CH <sub>3</sub> ) <sub>2</sub> (70)	316	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF- <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 1:1, -78°, 0.17 hr	CH <sub>3</sub> CO <sub>2</sub> H	A, C <sub>6</sub> H <sub>5</sub> CHORGe(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OR A: 71, B: 29, R = H (-) A: 83, B: 17, R = CH <sub>3</sub> (-) A: 73, B: 27, R = CH <sub>3</sub> (-) A: 70, B: 30, R = H (-)	128 128 128 128	
C <sub>6</sub> H <sub>5</sub> CHDOGe(CH <sub>3</sub> ) <sub>3</sub> S(+)	LDA, THF, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 25°, 48 hr	CH <sub>3</sub> I (CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> CH <sub>3</sub> CO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> CD(OH)Ge(CH <sub>3</sub> ) <sub>3</sub> S(-) (80)	608	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF- <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 1:1, -50°, 3 min	CH <sub>3</sub> CO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> CH(OH)Si(CH <sub>3</sub> ) <sub>3</sub> (95)	47	
	-78° -0° -78°	H <sub>2</sub> O	(79)	47	
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, 25°	CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )OSi(CH <sub>3</sub> ) <sub>3</sub> (-)	47	
	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>n</i> -C <sub>5</sub> H <sub>12</sub> , TMEDA, -23°, 3 hr	H <sub>2</sub> O CH <sub>3</sub> CO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> CH(OH)Si(CH <sub>3</sub> ) <sub>3</sub> (86)	128	
		CH <sub>3</sub> CO <sub>2</sub> H	A, C <sub>6</sub> H <sub>5</sub> CH(OH)Si(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH + C, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> A: 61, B: 13, C: 26 (-)	128	
		(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiCl	A, C <sub>6</sub> H <sub>5</sub> CH[OSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ]Si(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> + C, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> + D, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> A: 60, B: 16, C: 21, D: 3 (-)	128	
	LDA, THF, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 25°, 12 hr	CH <sub>3</sub> CO <sub>2</sub> H	A, C <sub>6</sub> H <sub>5</sub> CH(OH)Si(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH + C, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> A: 84, B: 14, C: 2 (-)	128	



TABLE X. ETHERS (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>10</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF- <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 1:1, -50°, <2 min	CH <sub>3</sub> I	A, C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )OSi(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH(OCH <sub>3</sub> )Si(CH <sub>3</sub> ) <sub>3</sub> + C, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>3</sub> + D, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> H <sub>5</sub> A: 91, B: 7, C: 1, D: 1 (-)	128	
			(CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiCl	A: 36, B: 62, C: 1, D: 1 (-) A, C <sub>6</sub> H <sub>5</sub> CH[OSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ]Si(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> + C, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> A: 96, B: 2, C: 2 (-)	128 128	
			CH <sub>3</sub> CO <sub>2</sub> H	A, C <sub>6</sub> H <sub>5</sub> CH(OH)Si(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH + C, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> A: 95, B: 1, C: 4 (-)	128	
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF- <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 1:1, -40°, 30 min	CH <sub>3</sub> I	A, C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )OSi(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH[Si(CH <sub>3</sub> ) <sub>3</sub> ]OCH <sub>3</sub> A: 99, B: 1 (-)	128 128	
			(CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> (CH <sub>3</sub> ) <sub>3</sub> SiCl	A: 40, B: 60 (-) C <sub>6</sub> H <sub>5</sub> CH[OSi(CH <sub>3</sub> ) <sub>3</sub> ]Si(CH <sub>3</sub> ) <sub>3</sub> (-)	128 128	
			CH <sub>3</sub> CO <sub>2</sub> H	A, C <sub>6</sub> H <sub>5</sub> CH(OH)Si(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH + C, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>3</sub> A: 97, B: 1, C: 2 (-)	128	
		C <sub>6</sub> H <sub>5</sub> CHDOSi(CH <sub>3</sub> ) <sub>3</sub> S(+)	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , -23°, 0.17 hr <i>t</i> -C <sub>4</sub> H <sub>9</sub> Li (1.5 eq), THF, -78° to -50°	CH <sub>3</sub> CO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH (-)	128
				CH <sub>3</sub> CO <sub>2</sub> H	A, C <sub>6</sub> H <sub>5</sub> CHDOH S(+) + B, C <sub>6</sub> H <sub>5</sub> CHDOSi(CH <sub>3</sub> ) <sub>3</sub> S(+) + C, C <sub>6</sub> H <sub>5</sub> CD(OH)Si(CH <sub>3</sub> ) <sub>3</sub> S(-) A: 3, B: 24, C: 73 (96) A, C <sub>6</sub> H <sub>5</sub> CD(CH <sub>3</sub> )OSi(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CD(OH)Si(CH <sub>3</sub> ) <sub>3</sub> A: 40, B: 60 (-)	603 603
		<i>n</i> -C <sub>5</sub> H <sub>11</sub> C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.2 eq), ether, -78°	H <sub>2</sub> O	<i>n</i> -C <sub>5</sub> H <sub>11</sub> CH=C=CHOC <sub>2</sub> H <sub>5</sub> (-)	273
				(CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> , -78°	<i>n</i> -C <sub>5</sub> H <sub>11</sub> C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> (-) <i>n</i> -C <sub>5</sub> H <sub>11</sub> CR=C=CHOC <sub>2</sub> H <sub>5</sub> A, R = CH <sub>3</sub> (80)	273
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>4</sub> , -78°	A, R = C <sub>2</sub> H <sub>5</sub> (100)			273		
(CH <sub>3</sub> ) <sub>3</sub> SiCl	A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (100)			273		
CH <sub>2</sub> O	<i>n</i> -C <sub>5</sub> H <sub>11</sub> C≡CCHROC <sub>2</sub> H <sub>5</sub> A, R = CH <sub>2</sub> OH (70) A, R = CH(OH)CH <sub>3</sub> (90) A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (60)			30 30 30		
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 1 hr ZnI <sub>2</sub> , THF, -70°, 1 hr	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.2 eq), ether, -78° <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 1 hr ZnI <sub>2</sub> , THF, -70°, 1 hr	CH <sub>3</sub> CHO	A, R = CH(OH)C≡CC <sub>5</sub> H <sub>11-n</sub> (80)	30		
		CH <sub>3</sub> COCH <sub>3</sub>	A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (85)	30		
		<i>n</i> -C <sub>5</sub> H <sub>11</sub> C≡CCHO	A, R = CH(OH)C <sub>6</sub> H <sub>4</sub> OCH <sub>3-x</sub> (78)	30		
<i>n</i> -C <sub>5</sub> H <sub>7</sub> C≡CCH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> [(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> ] <sub>2</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 1 hr ZnI <sub>2</sub> , THF, 70°, 1 hr NaNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq) <i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -15° <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -25°	H <sub>2</sub> O	HC≡CCH=CH <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (67)	183		
		H <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH(OH)C(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub> (35)	210		
		H <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH(OH)C(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub> (67)	212		
			(CH <sub>3</sub> ) <sub>2</sub> C=CHCH(OH)CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (14) + CH <sub>2</sub> =CHC(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CHO (10) + (CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CHO (8)			

TABLE X. ETHERS (Continued)

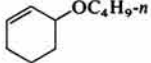
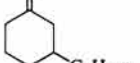





No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>10</sub> (Contd.)	[(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> ] <sub>2</sub> O	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -15°	H <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH(OH)C(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub> (-) + (CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> OH (-)	210
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, 25°	H <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=CHC <sub>5</sub> H <sub>11-n</sub> (-) A, (CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> CH(OH)CH=C(CH <sub>3</sub> ) <sub>2</sub> + B, (CH <sub>3</sub> ) <sub>2</sub> C=CHCH(OH)C(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub> + C, (CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> OH + D, (CH <sub>3</sub> ) <sub>2</sub> C=CHC <sub>5</sub> H <sub>11-n</sub> A: 1, B: 1 (-)	210
		<i>n</i> -C <sub>3</sub> H <sub>7</sub> Li (1.3 eq), TMEDA, C <sub>5</sub> H <sub>12</sub> , reflux, 17 hr	Hydrolysis	 (-)	203
	CH <sub>3</sub> OCH(CH <sub>3</sub> )C≡CCH <sub>2</sub> OC <sub>4</sub> H <sub>9-t</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -40° to -50°, 35 min	H <sub>2</sub> O	CH <sub>3</sub> CH=C=C=CHOC <sub>4</sub> H <sub>9-t</sub> <i>cis</i> : 1, <i>trans</i> : 4 (53)	170
	C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> C≡CCH <sub>2</sub> OC <sub>4</sub> H <sub>9-t</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , 50°, 1 hr	-	C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> CH=C=CHOC <sub>4</sub> H <sub>9-t</sub> + C <sub>2</sub> H <sub>5</sub> OCH=C=CHCH <sub>2</sub> OC <sub>4</sub> H <sub>9-t</sub> (75) CH <sub>3</sub> C≡CCH=CHOCH <sub>3</sub> (67)	495
	C <sub>2</sub> H <sub>5</sub> OCH(CH <sub>3</sub> )OCH(CH <sub>3</sub> )C≡CCH <sub>2</sub> OCH <sub>3</sub>	NaNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq), ether	NH <sub>4</sub> Cl	C <sub>2</sub> H <sub>5</sub> OCH=C=C(CH <sub>3</sub> )CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (80)	510
	C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> C≡CCH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li	CH <sub>3</sub> I	(CH <sub>3</sub> ) <sub>3</sub> SiCR=C=CHOC <sub>4</sub> H <sub>9-t</sub>	601
	(CH <sub>3</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> OC <sub>4</sub> H <sub>9-t</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -40°	CH <sub>3</sub> I	A, R = CH <sub>3</sub> (>60)	275
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -40°, then -5°, 1 hr	(CH <sub>3</sub> ) <sub>3</sub> SiCl H <sub>2</sub> O	A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (>60) A, (CH <sub>3</sub> ) <sub>3</sub> SiCR=C=CHOC <sub>4</sub> H <sub>9-t</sub> + B, (CH <sub>3</sub> ) <sub>3</sub> SiC≡CCHROC <sub>4</sub> H <sub>9-t</sub>	275
			CH <sub>3</sub> I (CH <sub>3</sub> ) <sub>3</sub> SiCl	A: 40, B: 60, R = H (-) A: (80), B: (5), R = CH <sub>3</sub> A: (>60), B: (0), R = Si(CH <sub>3</sub> ) <sub>3</sub>	272 272 272
C <sub>11</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> C≡CCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -60° to -30°	CH <sub>3</sub> OH	CH <sub>3</sub> C≡CCH(OH)C <sub>6</sub> H <sub>4</sub> CH <sub>3-o</sub> (46) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(OH)C≡CCH <sub>3</sub> (18)	510
	CH <sub>2</sub> =C(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> OCH=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , ether, TMEDA, -75°, 2 hr	H <sub>2</sub> O	CH <sub>2</sub> =C(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11-n</sub> (89)	202
	C <sub>6</sub> H <sub>5</sub> C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub>	-	C <sub>6</sub> H <sub>5</sub> CH=C=CHOC <sub>2</sub> H <sub>5</sub> (-)	518
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -75°, 15 min	[(CH <sub>3</sub> ) <sub>3</sub> N] <sub>3</sub> PO, (CH <sub>3</sub> ) <sub>3</sub> SiCl (2 eq)	C <sub>6</sub> H <sub>5</sub> [(CH <sub>3</sub> ) <sub>3</sub> Si]C=C=C[Si(CH <sub>3</sub> ) <sub>3</sub> ]OC <sub>2</sub> H <sub>5</sub> (70)	124
	C <sub>6</sub> H <sub>5</sub> C≡CCH(CH <sub>3</sub> )OCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -20°, 10 min	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, C <sub>2</sub> H <sub>5</sub> I, -20° ClCH <sub>2</sub> OCH <sub>3</sub> , -30°	C <sub>6</sub> H <sub>5</sub> C(C <sub>2</sub> H <sub>5</sub> )=C=C(CH <sub>3</sub> )OCH <sub>3</sub> (85)	274
			(CH <sub>3</sub> ) <sub>3</sub> SiCl	CH <sub>3</sub> OCH <sub>2</sub> C(C <sub>6</sub> H <sub>5</sub> )=C=C(CH <sub>3</sub> )OCH <sub>3</sub> (-)	274
			CH <sub>3</sub> OH	(CH <sub>3</sub> ) <sub>3</sub> SiC(C <sub>6</sub> H <sub>5</sub> )=C=C(CH <sub>3</sub> )OCH <sub>3</sub> (-)	274
	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )OCH <sub>2</sub> CH=CH <sub>2</sub>	CH <sub>3</sub> Li, THF, ether	CH <sub>3</sub> OH	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )OCH <sub>2</sub> CH=CH <sub>2</sub> (42) + A, C <sub>6</sub> H <sub>5</sub> C(OH)(CH <sub>3</sub> )CH <sub>2</sub> CH=CH <sub>2</sub> + B, CH <sub>2</sub> =CHCH(OH)C <sub>6</sub> H <sub>4</sub> C <sub>2</sub> H <sub>5-o</sub> + C, C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )CH(OH)CH=CH <sub>2</sub> A: 3, B: 16, C: 1 (-)	209
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH(CH <sub>3</sub> )CH=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80°	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> CH=CH <sub>2</sub> (-)	212
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> CH=CHCH <sub>3</sub>	CH <sub>3</sub> Li, THF, ether	CH <sub>3</sub> OH	<i>trans</i> C <sub>6</sub> H <sub>5</sub> CH(OH)CH(CH <sub>3</sub> )CH=CH <sub>2</sub>	209
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> CH=CHCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80°	H <sub>2</sub> O	<i>erythro</i> : 2, <i>threo</i> : 1 (-)	212
	<i>cis</i> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> CH=CHCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80°	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH(OH)CH(CH <sub>3</sub> )CH=CH <sub>2</sub> (-)	212
	<i>trans</i> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> CH=CHCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80°	-	<i>threo</i> C <sub>6</sub> H <sub>5</sub> CH(OH)CH(CH <sub>3</sub> )CH=CH <sub>2</sub>	212
	<i>trans</i> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> CH=CHCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80°	-	<i>erythro</i> : 1, <i>threo</i> : 1 (-)	211
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O 	CH <sub>3</sub> Li (2 eq), THF, room temperature, 24 hr	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH(OH)  (75) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH (13)	488
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> 	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Li, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , room temperature, 96 hr	H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub>  + B, C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub>  + C, C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> A: 59, B: 57, C: 4 (-)	488

TABLE X. ETHERS (Continued)





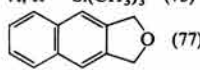
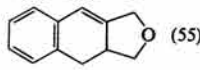
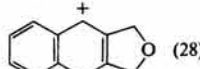

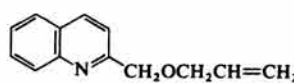
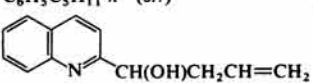

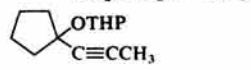
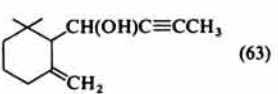
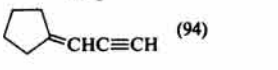
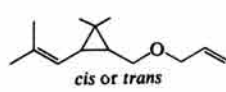
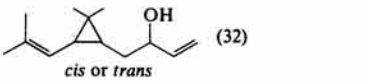

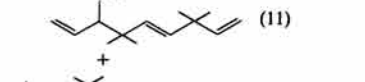
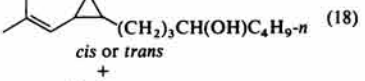
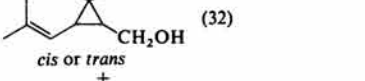
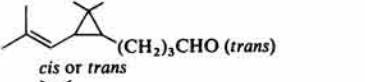
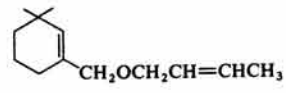
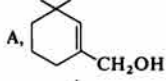

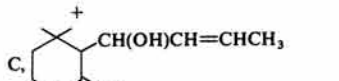
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
140	C <sub>11</sub> (Contd.)				
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> - 	CH <sub>3</sub> Li (2 eq), THF, room temperature, 24 hr	H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> - 	488
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70° to -20°	H <sub>2</sub> O	B, C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> A: 94, B: 6 (-) A, C <sub>6</sub> H <sub>5</sub> CH(OH)CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH + C, C <sub>2</sub> H <sub>5</sub> CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> CHO- <i>p</i> + D, C <sub>2</sub> H <sub>5</sub> CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> CHO- <i>o</i> + E, C <sub>6</sub> H <sub>5</sub> COCH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub> A: 70, B: 20, C: 5, D + E: 5 (-)	199
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF-ether, 2.6:1, -74°, 30 min	H <sub>2</sub> O, 25°	C <sub>6</sub> H <sub>5</sub> COCD(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub> (after oxidation) (0.29 D) (-) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCD(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub> (0.3 D) (-) C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>t</i> (45) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH (4) + C <sub>6</sub> H <sub>5</sub> CHO (7) + polymers (14)	174
	 -C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub> Li (5 eq), THF, 25°, 48 hr KNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq)	NH <sub>4</sub> Cl H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CHDOC <sub>4</sub> H <sub>9</sub> - <i>t</i> (0.1 D) (-) C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>t</i> (5)  =CHC≡CH (91)	174 487 183
	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )OSi(CH <sub>3</sub> ) <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF- <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 1:1, -30°, 13 hr LDA, THF, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 25°, 12 hr	CH <sub>3</sub> CO <sub>2</sub> H CH <sub>3</sub> CO <sub>2</sub> H	A, C <sub>6</sub> H <sub>5</sub> C(OH)(CH <sub>3</sub> )Si(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>3</sub> + C, C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )OSi(CH <sub>3</sub> ) <sub>3</sub> A: 29, B: 56, C: 5 (75) A: 2, B: 4, C: 94 (-)	128 128
	CH <sub>3</sub> C≡CC(CH <sub>3</sub> ) <sub>2</sub> OTHP <i>n</i> -C <sub>5</sub> H <sub>11</sub> (CH <sub>3</sub> )C=C=CHOC <sub>2</sub> H <sub>5</sub>	KNH <sub>2</sub> (3 eq), NH <sub>3</sub> (liq) <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), ether, 0°	H <sub>2</sub> O (CH <sub>3</sub> ) <sub>3</sub> SiCl	HC≡CCH=C(CH <sub>3</sub> ) <sub>2</sub> (85) <i>n</i> -C <sub>5</sub> H <sub>11</sub> (CH <sub>3</sub> )C=C=CROC <sub>2</sub> H <sub>5</sub> A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (100) A, R = CH <sub>3</sub> (100)	183 273 273
	C <sub>2</sub> H <sub>5</sub> OCH(CH <sub>3</sub> )C≡CCH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , 50°, 1 hr	CH <sub>3</sub> I	C <sub>2</sub> H <sub>5</sub> OCH(CH <sub>3</sub> )CH=C=CHOC <sub>4</sub> H <sub>9</sub> - <i>t</i> (70)	275
	CH <sub>3</sub> OCH(C <sub>2</sub> H <sub>5</sub> )C≡CCH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -40° to -50°, 35 min	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> CH=C=C=CHOC <sub>4</sub> H <sub>9</sub> - <i>t</i> <i>cis</i> : 1, <i>trans</i> : 4 (63)	170
	C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> C≡CCH(CH <sub>3</sub> )OC <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , 50°, 1 hr	—	C <sub>2</sub> H <sub>5</sub> OCH=C=CHCH(CH <sub>3</sub> )OC <sub>4</sub> H <sub>9</sub> - <i>t</i> (70)	275
(CH <sub>3</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> OTHP	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 1 hr, ZnI <sub>2</sub> , THF, -70°, 1 hr	C <sub>6</sub> H <sub>5</sub> CHO	(CH <sub>3</sub> ) <sub>3</sub> SiC≡CCH[CH(OH)(C <sub>6</sub> H <sub>5</sub> )]OTHP (55)	30	
141	C <sub>2</sub> H <sub>5</sub> OCH(CH <sub>3</sub> )OC(CH <sub>3</sub> ) <sub>2</sub> C≡CCH <sub>2</sub> OCH <sub>3</sub> <i>n</i> -C <sub>8</sub> H <sub>17</sub> OCH <sub>2</sub> CH=CH <sub>2</sub>	NaNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq), ether <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 25° to 35°, 85 min	NH <sub>4</sub> Cl H <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=C=C=CHOCH <sub>3</sub> (64) A, <i>n</i> -C <sub>8</sub> H <sub>17</sub> OH + B, <i>n</i> -C <sub>8</sub> H <sub>17</sub> OCH=CHCH <sub>3</sub> <i>cis</i> A: 77, B: 23 (-)	510 354
	(CH <sub>3</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )OC <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether	CH <sub>3</sub> I (CH <sub>3</sub> ) <sub>3</sub> SiCl	(CH <sub>3</sub> ) <sub>3</sub> SiC(CH <sub>3</sub> )=C=C(CH <sub>3</sub> )OC <sub>4</sub> H <sub>9</sub> - <i>t</i> (25) [(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=C(CH <sub>3</sub> )OC <sub>4</sub> H <sub>9</sub> - <i>t</i> (25)	272 272
	(CH <sub>3</sub> ) <sub>3</sub> SiC(CH <sub>3</sub> )=C=CHOC <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -40°, then -10°, 1 hr	H <sub>2</sub> O CH <sub>3</sub> I (CH <sub>3</sub> ) <sub>3</sub> SiCl	(CH <sub>3</sub> ) <sub>3</sub> SiC(CH <sub>3</sub> )=C=CROC <sub>4</sub> H <sub>9</sub> - <i>t</i> A, R = H (75) A, R = CH <sub>3</sub> (75) A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (75)	272, 275 272 272
	C <sub>12</sub>			 (77)	342
	C <sub>6</sub> H <sub>5</sub> C≡CCH <sub>2</sub> OCH <sub>2</sub> CH=CH <sub>2</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, 55°, 22 hr	—	 (55) +  (28)	342

TABLE X. ETHERS (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>12</sub> (Contd.)		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> , -30°, then 20°	—		562
	C <sub>6</sub> H <sub>5</sub> C≡CCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OC(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, 25° -20°	— H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH=C=C(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> (—) A, C <sub>6</sub> H <sub>5</sub> CH(OH)C(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> A: 23, B: 77 (—) A: 17, B: 83 (—)	509 210 210
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH(CH <sub>3</sub> )CH=CHCH <sub>3</sub> <i>trans</i> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, 0° <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80° -80°, then -25° -80°, then 23° -25° 25° -10°	H <sub>2</sub> O H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH(OH)CH(CH <sub>3</sub> )CH=CHCH <sub>3</sub> <i>cis</i> : 17 <i>trans</i> : 83 (—) A, C <sub>6</sub> H <sub>5</sub> CH(OH)C(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> A: 8, B: 1 (—) A: 6.5, B: 1 (—) A: 6, B: 1 (—) A: 1, B: 1.4 (—) A: 95, B: 5 (—) A: 98, B: 2 (—)	211 212 212 212 210 210
		KNH <sub>2</sub> (3 eq), NH <sub>3</sub> (liq), <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>14</sub> , ether, TMEDA, 5°, 25°, 16 hr	H <sub>2</sub> O H <sub>2</sub> O	HC≡CCH=C(CH <sub>3</sub> )CH=CH <sub>2</sub> (70) 	183 202
				+ 	
				+ 	
	CH <sub>3</sub> C≡CCH(C <sub>3</sub> H <sub>7-<i>n</i>})OTHP CH<sub>3</sub>C≡CC(CH<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)OTHP (CH<sub>3</sub>)<sub>3</sub>SiC≡CCH<sub>2</sub>OCH<sub>2</sub>C≡CSi(CH<sub>3</sub>)<sub>3</sub></sub>	KNH <sub>2</sub> (3 eq), NH <sub>3</sub> (liq) KNH <sub>2</sub> (3 eq), NH <sub>3</sub> (liq) <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA, -80°	H <sub>2</sub> O H <sub>2</sub> O H <sub>2</sub> O	HC≡CCH=CHC <sub>3</sub> H <sub>7-<i>n</i></sub> (78) HC≡CCH=C(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> ) (87) (CH <sub>3</sub> ) <sub>3</sub> SiC≡CCH(OH)C[Si(CH <sub>3</sub> ) <sub>3</sub> ]=C=CH <sub>2</sub> (52)	183 183 440
	CH <sub>3</sub> OCH(C <sub>3</sub> H <sub>7-<i>i</i>})C≡CCH<sub>2</sub>OC<sub>4</sub>H<sub>9-<i>t</i></sub></sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , 50°, 1 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -40° to -50°, 35 min	— H <sub>2</sub> O	CH <sub>3</sub> OCH(C <sub>3</sub> H <sub>7-<i>i</i>})CH=C=CHOC<sub>4</sub>H<sub>9-<i>t</i></sub> (76) <i>i</i>-C<sub>3</sub>H<sub>7</sub>CH=C=C=CHOC<sub>4</sub>H<sub>9-<i>t</i></sub> <i>cis</i>: 1, <i>trans</i>: 4 (74)</sub>	495 170
	C <sub>2</sub> H <sub>5</sub> OCH(C <sub>2</sub> H <sub>5</sub> )C≡CCH <sub>2</sub> OC <sub>4</sub> H <sub>9-<i>t</i></sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , 50°, 1 hr	—	C <sub>2</sub> H <sub>5</sub> OCH(C <sub>2</sub> H <sub>5</sub> )CH=C=CHOC <sub>4</sub> H <sub>9-<i>t</i></sub> (75)	495
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> OCH <sub>2</sub> C≡CCH <sub>2</sub> OC <sub>4</sub> H <sub>9-<i>n</i></sub> C <sub>2</sub> H <sub>5</sub> OCH(CH <sub>3</sub> )OC(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )C≡CCH <sub>2</sub> OCH <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CO	NaNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq) NaNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq), ether (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SiK, ether, room temperature	H <sub>2</sub> O NH <sub>4</sub> Cl C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	HC≡CCH=CHOC <sub>4</sub> H <sub>9-<i>n</i></sub> (78) (C <sub>2</sub> H <sub>5</sub> )(CH <sub>3</sub> )C=C=CHOC <sub>4</sub> H <sub>9</sub> (60) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )OSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (16)	183 510 568
	(CH <sub>3</sub> ) <sub>3</sub> SiCl CO <sub>2</sub> , H <sub>3</sub> O <sup>+</sup> CH <sub>2</sub> O, H <sup>+</sup>		(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C[Si(CH <sub>3</sub> ) <sub>3</sub> ]OSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (25) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH)CO <sub>2</sub> H (8) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> OH (—)	568 568 568	
C <sub>13</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (excess), THF, 0°, then room temperature, 48 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.5 eq), THF, room temperature, 48 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, (CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub>	H <sub>2</sub> O H <sub>2</sub> O —		201
	C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>			C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>6</sub> H <sub>5</sub> (98) C <sub>6</sub> H <sub>5</sub> OLi (81) + (CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub> (—) +	201
				+ 	565
		CH <sub>3</sub> Li, CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> -THF, 1:1 <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether-C <sub>6</sub> H <sub>10</sub> , 8:15, 25°, 10 hr	H <sub>2</sub> O —	C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>6</sub> H <sub>5</sub> (80) C <sub>6</sub> H <sub>5</sub> OH (68) +	201 565
				+ 	
			+ C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> <i>trans</i> (9)		

TABLE X. ETHERS (Continued)

No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
$C_{13}$ (Contd.) $C_6H_5OCH_2C_6H_5$	$n-C_4H_9Li, (CH_3)_2C=CH_2,$ $-70^\circ$	—	$C_6H_5OH$ (81) +  $C_6H_5$ (0.5) + $C_6H_5CH_2CH(C_6H_5)C_4H_9-n$ (3) + $C_6H_5C_5H_{11-n}$ (0.7)	565
 $n-C_4H_9C\equiv CCH_2OC_6H_5$ $C_6H_5C\equiv CCH(C_2H_5)OC_2H_5$ $C_6H_5C\equiv CCH(OCH_3)C_3H_7-i$	$NaNH_2, NH_3$ (liq), 2 hr $NaNH_2$ (2 eq), $NH_3$ (liq) $t-C_4H_9OK, CH_3SOCH_3$ $n-C_4H_9Li$ , ether, $-20^\circ$ , 10 min	— $H_2O$ — $H_2O$ $D_2O$ $ClCH_2CH_2N(C_2H_5)_2,$ $[(CH_3)_2N]_3PO,$ $-20^\circ$ , then reflux 1 then reflux 1 hr	 (66) $HC\equiv CCH=CHC_3H_7-n$ (70) $C_6H_5CH=C(C_2H_5)OC_2H_5$ (—) $C_6H_5C(R)=C=C(OCH_3)C_3H_7-i$ A, R = H (—) A, R = D (—) A, R = $CH_2CH_2N(C_2H_5)_2$ (—)	213 183 274 274 274 274
 $CH_2OCH_2C\equiv CCH_3$  $OTHP$ $C\equiv CCH_3$	$n-C_4H_9Li, TMEDA$ , ether, $-75^\circ$ , 2 hr, then $-30^\circ$ , 2 hr $KNH_2$ (3 eq), $NH_3$ (liq)	$H_2O$ $H_2O$	 (63)  (94)	567 183
 <i>cis or trans</i>	$n-C_4H_9Li, THF, -20^\circ$	$H_2O$	 (32) <i>cis or trans</i> +  (17) +  (11) +  (18) <i>cis or trans</i> +  (32) <i>cis or trans</i> +  (trans)	214
 $CH_2OCH_2CH=CHCH_3$	$n-C_4H_9Li$ , ether, TMEDA, $-80^\circ$ to $-25^\circ$ , 165 min	$H_2O$	A,  $CH_2OH$ + B,  $CH(OH)CH(CH_3)CH=CH_2$ + C,  $CH(OH)CH=CHCH_3$ $CH_2$ A: 12, B: 59, C: 29 (70)	567

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TABLE X. ETHERS (Continued)

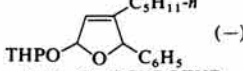


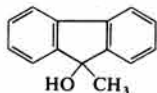
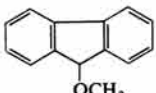
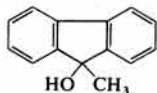
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
146	C <sub>13</sub> (Contd.) C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), <i>n</i> -C <sub>5</sub> H <sub>12</sub> , room temperature, 44 hr	H <sup>+</sup>	A, C <sub>6</sub> H <sub>5</sub> CH(OH)Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> + C, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH 31 A: 75, B: 18, C: 7 (-) A: (96), B(0.8), C(3)	31 31
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li (5 eq), <i>n</i> -C <sub>5</sub> H <sub>12</sub> , room temperature, 144 hr	H <sup>+</sup>	A: (67) A: 65, B: 13, C: 22 (-)	31 128
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>n</i> -C <sub>5</sub> H <sub>12</sub> , room temperature, 144 hr	(CH <sub>3</sub> ) <sub>3</sub> SiCl, then H <sup>+</sup> CH <sub>3</sub> CO <sub>2</sub> H	A: (67) A: 65, B: 13, C: 22 (-)	31 128
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 25°, 0.13 hr	CH <sub>3</sub> CO <sub>2</sub> H	A, C <sub>6</sub> H <sub>5</sub> CH(OH)Si(CH <sub>3</sub> ) <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i> A: 54, B: 46 (-) A: 70, B: 30 (-)	128 128
		LDA, THF, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 25°, 12 hr	CH <sub>3</sub> CO <sub>2</sub> H	A: 64, B: 36 (-)	128
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF- <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 1:1, -23°, 1.33 hr	CH <sub>3</sub> CO <sub>2</sub> H	A: 85, B: 15 (-)	128
	<i>n</i> -C <sub>5</sub> H <sub>11</sub> C≡CCH <sub>2</sub> OTHP	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>5</sub> H <sub>12</sub> , TMEDA, 25°, 7 hr	CH <sub>3</sub> CO <sub>2</sub> H	A, <i>n</i> -C <sub>5</sub> H <sub>11</sub> CH=C=CHOTHP + B, <i>n</i> -C <sub>5</sub> H <sub>11</sub> C≡CCH <sub>2</sub> OTHP A: 7, B: 3 (-)	381
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 25°, 2 hr	CH <sub>3</sub> CO <sub>2</sub> H	<i>n</i> -C <sub>5</sub> H <sub>11</sub> C≡CCH[CH(OH)C <sub>6</sub> H <sub>5</sub> ]OTHP erythro: 4, threo: 1 (-)	30
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -25°, 2.5 hr	CH <sub>3</sub> OH, H <sub>2</sub> O	 (-)	30
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 1 hr	C <sub>6</sub> H <sub>5</sub> CHO, -70°, then H <sub>2</sub> O, H <sup>+</sup>	THPO <i>n</i> -C <sub>5</sub> H <sub>11</sub> C≡CCHROTHP A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (60)	30
C <sub>6</sub> H <sub>5</sub> CH[Si(CH <sub>3</sub> ) <sub>3</sub> ]OSi(CH <sub>3</sub> ) <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>n</i> -C <sub>5</sub> H <sub>12</sub> , TMEDA, 25°, 0.67 hr	CH <sub>3</sub> COCH <sub>3</sub> CH <sub>2</sub> O <i>n</i> -C <sub>5</sub> H <sub>11</sub> C≡CCHO CH <sub>3</sub> CO <sub>2</sub> H	A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (52) A, R = CH <sub>2</sub> OH (63) A, R = CH(OH)C≡CC <sub>5</sub> H <sub>11</sub> - <i>n</i> (80) A, C <sub>6</sub> H <sub>5</sub> CH[Si(CH <sub>3</sub> ) <sub>3</sub> ]OSi(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH[Si(CH <sub>3</sub> ) <sub>3</sub> ]OH A: 96, B: 4 (-) A: 90, B: 10 (-)	30 30 30 128 128	
	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF- <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 1:1, -23°, 0.5 hr	CH <sub>3</sub> CO <sub>2</sub> H	C <sub>2</sub> H <sub>5</sub> OCH(C <sub>3</sub> H <sub>7</sub> - <i>i</i> )CH=C=CHOC <sub>4</sub> H <sub>9</sub> - <i>t</i> (70)	495	
	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , 50°, 1 hr	—	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C=C=C=CHOCH <sub>3</sub> (62) <i>t</i> -C <sub>4</sub> H <sub>9</sub> OC(CH <sub>3</sub> )=C=CRCH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> A, R = H (85) A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (75) A, R = CH <sub>3</sub> (85) A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (70) <i>n</i> -C <sub>5</sub> H <sub>11</sub> [(CH <sub>3</sub> ) <sub>3</sub> Si]C=C=CROC <sub>2</sub> H <sub>5</sub> A, R = C <sub>2</sub> H <sub>5</sub> (71) A, R = C <sub>2</sub> H <sub>5</sub> (70) A, R = CH <sub>3</sub> (100) A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (78) A, R = C <sub>2</sub> H <sub>5</sub> (61)	510 601 601 601 273 273 273 273 273	
C <sub>2</sub> H <sub>5</sub> OCH(CH <sub>3</sub> )OC(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C≡CCH <sub>2</sub> OCH <sub>3</sub> <i>t</i> -C <sub>4</sub> H <sub>9</sub> OCH(CH <sub>3</sub> )C≡CCH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	NaNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq) <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li	NH <sub>4</sub> Cl H <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C=C=C=CHOCH <sub>3</sub> (62) <i>t</i> -C <sub>4</sub> H <sub>9</sub> OC(CH <sub>3</sub> )=C=CRCH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> A, R = H (85) A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (75) A, R = CH <sub>3</sub> (85) A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (70) <i>n</i> -C <sub>5</sub> H <sub>11</sub> [(CH <sub>3</sub> ) <sub>3</sub> Si]C=C=CROC <sub>2</sub> H <sub>5</sub> A, R = C <sub>2</sub> H <sub>5</sub> (71) A, R = C <sub>2</sub> H <sub>5</sub> (70) A, R = CH <sub>3</sub> (100) A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (78) A, R = C <sub>2</sub> H <sub>5</sub> (61)	510 601 601 601 273 273 273 273 273	
	<i>n</i> -C <sub>5</sub> H <sub>11</sub> [(CH <sub>3</sub> ) <sub>3</sub> Si]C=C=CHOC <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), ether, 0°	(CH <sub>3</sub> ) <sub>3</sub> SiCl CH <sub>3</sub> I CH <sub>3</sub> COCH <sub>3</sub> C <sub>2</sub> H <sub>5</sub> Br	<i>n</i> -C <sub>5</sub> H <sub>11</sub> [(CH <sub>3</sub> ) <sub>3</sub> Si]C=C=CROC <sub>2</sub> H <sub>5</sub> A, R = C <sub>2</sub> H <sub>5</sub> (71) A, R = C <sub>2</sub> H <sub>5</sub> (70) A, R = CH <sub>3</sub> (100) A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (78) A, R = C <sub>2</sub> H <sub>5</sub> (61)	273 273 273 273 273
147	[(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHOC <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), ether-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 1:1, 0°	C <sub>2</sub> H <sub>5</sub> I (CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> (CH <sub>3</sub> ) <sub>3</sub> SiCl C <sub>2</sub> H <sub>5</sub> Br	[(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CROC <sub>4</sub> H <sub>9</sub> - <i>t</i> A, R = H (60) A, R = CH <sub>3</sub> (70-85) A, R = CH <sub>2</sub> OCH <sub>3</sub> (70) A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (70-85) A, R = CH(OH)C <sub>3</sub> H <sub>7</sub> - <i>i</i> (70) A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (70-85) A, R = C(OH)(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (72)	272 272, 275 272 272, 275 272 272, 275 272
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -40°, then 10°, 1 hr	H <sub>2</sub> O	A, R = C(OH)(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (72)	272
		CH <sub>3</sub> I CH <sub>3</sub> OCH <sub>2</sub> Cl (CH <sub>3</sub> ) <sub>3</sub> SiCl <i>i</i> -C <sub>3</sub> H <sub>7</sub> CHO (CH <sub>3</sub> ) <sub>2</sub> CO (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CO		A, R =  (-)	272
		C <sub>6</sub> H <sub>5</sub> Li (1 eq), ether	H <sub>2</sub> O	 (24)	93
C <sub>14</sub>		C <sub>6</sub> H <sub>5</sub> Li (1 eq), ether	H <sub>2</sub> O	 (24)	93

TABLE X. ETHERS (Continued)

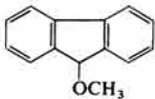
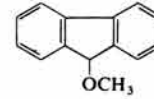
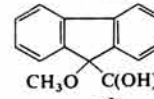
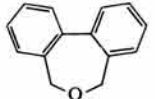
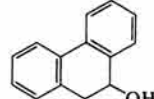
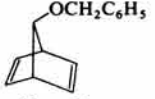
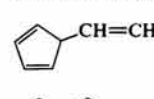
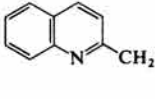
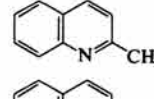
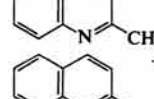
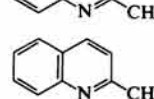
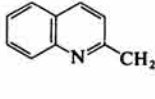
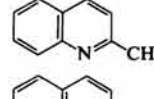
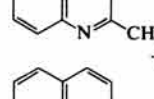
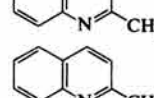
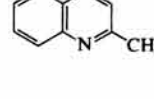
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>14</sub> (Contd.)		C <sub>6</sub> H <sub>5</sub> Li (1 eq), ether, room temperature, 24 hr	H <sub>2</sub> O	 (96)	93
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	 (47)	93
		C <sub>6</sub> H <sub>5</sub> Li, ether	H <sub>2</sub> O	 (77)	604
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> Li (5 eq), THF-CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , 1:1, room temperature, 48 hr	NH <sub>4</sub> Cl	A, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(OH)C <sub>6</sub> H <sub>5</sub> + B, C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>3</sub> A: 75, B: 25 (-)	487
		CH <sub>3</sub> Li (5 eq), THF, room temperature, 48 hr		A: 82, B: 18 (-)	487
		C <sub>6</sub> H <sub>5</sub> Li (1 eq), ether, room temperature, 40 hr	H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> + C, polymers	173
		n-C <sub>4</sub> H <sub>9</sub> Li (2.6 eq), ether, room temperature, 40 hr	CH <sub>3</sub> OH	A + B (74), C (15) C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (44)	208
		KNH <sub>2</sub> (2 eq), NH <sub>3</sub> , ether	—	C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (61-67) + C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> (16) + C <sub>6</sub> H <sub>5</sub> CONH <sub>2</sub> (14)	208
		KNH <sub>2</sub> (1 eq)	—	C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (51) + C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> (22) + C <sub>6</sub> H <sub>5</sub> CHO (28)	208
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (1 eq), ether, 5 hr	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH)CH <sub>3</sub> (23) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOCH <sub>3</sub> (13)	93
		CH <sub>3</sub> Li (excess), THF-ether, 1:1, room temperature	H <sub>2</sub> O	 (—)	189
		n-C <sub>4</sub> H <sub>9</sub> Li, THF, -25°, 2 hr	H <sub>2</sub> O	 (—)	213
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 2 hr	—	 (78) +  (14)	213
		n-C <sub>4</sub> H <sub>9</sub> Li, THF, -25°, 2 hr	H <sub>2</sub> O	 (90)	213
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 2 hr	—	 (74) +  (22)	213
		n-C <sub>4</sub> H <sub>9</sub> Li (4 eq), THF, -25°	H <sub>2</sub> O	 (90)	213

TABLE X. ETHERS (Continued)

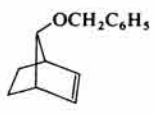
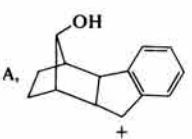
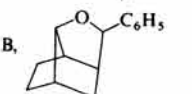
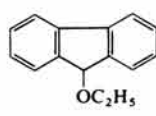
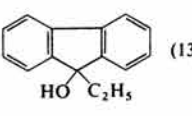
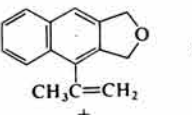
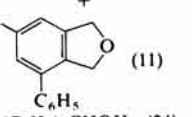
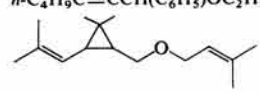

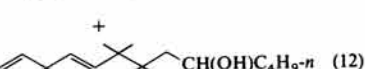
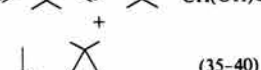
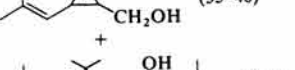
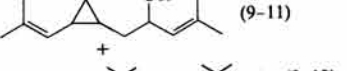
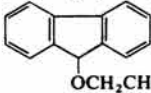
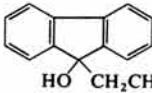
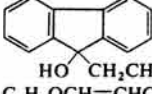
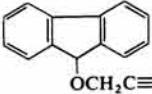
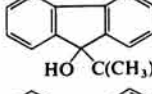
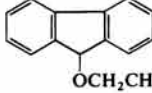
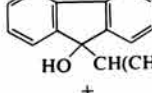
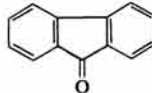
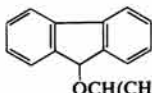
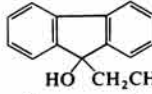
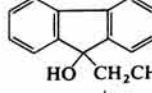
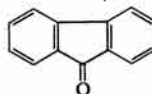
No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
150 C <sub>14</sub> (Contd.) 	CH <sub>3</sub> Li (excess), THF-ether, 1:1, room temperature	H <sub>2</sub> O	A,  + B, 	189
C <sub>6</sub> H <sub>5</sub> C≡CCH(C <sub>3</sub> H <sub>7-n</sub> )OC <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> C≡CCH(C <sub>3</sub> H <sub>7-i</sub> )OC <sub>2</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , room temperature, 30 min	—	A: 1, B: 1 (52) C <sub>6</sub> H <sub>5</sub> CH=C=C(OC <sub>2</sub> H <sub>5</sub> )C <sub>3</sub> H <sub>7-n</sub> (—) C <sub>6</sub> H <sub>5</sub> CH=C=C(OC <sub>2</sub> H <sub>5</sub> )C <sub>3</sub> H <sub>7-i</sub> (67)	509 494
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> C≡CCH <sub>2</sub> ) <sub>2</sub> O <i>n</i> -C <sub>4</sub> H <sub>9</sub> C≡CCH <sub>2</sub> OCH <sub>2</sub> C≡COC <sub>4</sub> H <sub>9-n</sub>	KNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq) NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	H <sub>2</sub> O H <sub>2</sub> O	HC≡CCH=CHC <sub>3</sub> H <sub>7-n</sub> (—) HC≡CCH=CHC <sub>3</sub> H <sub>7-n</sub> (—) + C <sub>4</sub> H <sub>9</sub> C≡CCH <sub>2</sub> OH (—)	183 183
CH <sub>3</sub> OCH(C <sub>3</sub> H <sub>11-n</sub> )C≡CCH <sub>2</sub> OC <sub>4</sub> H <sub>9-t</sub> <i>i</i> -C <sub>3</sub> H <sub>7</sub> OCH(C <sub>3</sub> H <sub>7-i</sub> )C≡CCH <sub>2</sub> OC <sub>4</sub> H <sub>9-t</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -40° to -50°, 35 min <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , 50°, 1 hr	H <sub>2</sub> O —	<i>n</i> -C <sub>3</sub> H <sub>11</sub> CH=C=C=CHOC <sub>4</sub> H <sub>9-t</sub> <i>cis</i> : 1, <i>trans</i> : 4 (54) <i>i</i> -C <sub>3</sub> H <sub>7</sub> OCH(C <sub>3</sub> H <sub>7-i</sub> )CH=C=CHOC <sub>4</sub> H <sub>9-t</sub> (70)	170 495
151 C <sub>15</sub> 	C <sub>6</sub> H <sub>5</sub> Li (1 eq), ether	H <sub>2</sub> O	 (13)	603
CH <sub>2</sub> =C(CH <sub>3</sub> )C≡CCH <sub>2</sub> OCH <sub>2</sub> C≡CC <sub>6</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, room temperature, overnight	—	 (55) +  (11)	342
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOCH <sub>2</sub> H <sub>5</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Na	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOH (24) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH)C <sub>2</sub> H <sub>5</sub> (44) + C <sub>2</sub> H <sub>4</sub> (24) + C <sub>3</sub> H <sub>8</sub> (110) C <sub>6</sub> H <sub>5</sub> CH=C=C(OC <sub>2</sub> H <sub>5</sub> )CH <sub>2</sub> C <sub>3</sub> H <sub>7-i</sub> (75)	175, 176
C <sub>6</sub> H <sub>5</sub> C≡CCH(OC <sub>2</sub> H <sub>5</sub> )CH <sub>2</sub> C <sub>3</sub> H <sub>7-i</sub> <i>n</i> -C <sub>4</sub> H <sub>9</sub> C≡CCH(C <sub>6</sub> H <sub>5</sub> )OC <sub>2</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , room temperature, 30 min <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub>	—	<i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=C=C(OC <sub>2</sub> H <sub>5</sub> )C <sub>6</sub> H <sub>5</sub> (—)	494 509
151 	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -20°	H <sub>2</sub> O	 (18) +  (12) +  (35-40) +  (9-11) +  (9-10)	214



TABLE X. ETHERS (Continued)

No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>15</sub> (Contd.)	CH <sub>3</sub> C≡CC(C <sub>3</sub> H <sub>7-n</sub> ) <sub>2</sub> OTHP <i>n</i> -C <sub>12</sub> H <sub>25</sub> OCH <sub>2</sub> CH=CH <sub>2</sub>	KNH <sub>2</sub> (3 eq), NH <sub>3</sub> (liq) <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , -33, 6 hr reflux, 2 hr	H <sub>2</sub> O D <sub>2</sub> O	HC≡CCH=C(C <sub>3</sub> H <sub>7-n</sub> ) <sub>2</sub> (88) <i>n</i> -C <sub>12</sub> H <sub>25</sub> OCH=CHCH <sub>3</sub> <i>cis</i> (88) A, <i>n</i> -C <sub>12</sub> H <sub>25</sub> OH + B, <i>n</i> -C <sub>12</sub> H <sub>25</sub> CH <sub>2</sub> CH=CH <sub>2</sub> A: 48, B: 52 (-)	183 353, 354 353, 354
	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OCH[Si(CH <sub>3</sub> ) <sub>3</sub> ]C≡CCH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li	H <sub>2</sub> O (CH <sub>3</sub> ) <sub>3</sub> SiCl CH <sub>3</sub> COCH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> O[Si(CH <sub>3</sub> ) <sub>3</sub> ]=C=CRCH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> A, R = H (70) A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (75) A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (70)	601 601 601
C <sub>16</sub>	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> C≡CCH <sub>2</sub> OC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i> 	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, 120°, 15 hr C <sub>6</sub> H <sub>5</sub> Li (1.1 eq), ether, -10° <i>n</i> -C <sub>4</sub> H <sub>9</sub> ONa, <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH, 120°, 2 hr	— H <sub>2</sub> O —	HC≡CCH=CHOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i> (-)  (80) HO CH <sub>2</sub> CH=CH <sub>2</sub>  (-) HO CH <sub>2</sub> CH=CH <sub>2</sub>	449 603 362
	C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> C≡CCH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CH=CHCH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub> <i>cis</i> C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CH=CHCH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub> <i>trans</i> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOGe(CH <sub>3</sub> ) <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, 120°, 15 hr <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, 120°, 15 hr <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, 120°, 15 hr <i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-C <sub>5</sub> H <sub>12</sub> , 1:1, -20°, 2 hr	— — — CH <sub>3</sub> CO <sub>2</sub> H CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> OCH=CHCH=CHOC <sub>6</sub> H <sub>5</sub> (-) CH <sub>2</sub> =CHCH=CHOC <sub>6</sub> H <sub>5</sub> (-) CH <sub>2</sub> =CHCH=CHOC <sub>6</sub> H <sub>5</sub> (-) A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH)Ge(CH <sub>3</sub> ) <sub>3</sub> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOH A: 70, B: 30 (-) A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OCH <sub>3</sub> )Ge(CH <sub>3</sub> ) <sub>3</sub> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOCH <sub>3</sub> A: 73, B: 27 (-)	449 449 449 128 128
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOSi(CH <sub>3</sub> ) <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-C <sub>5</sub> H <sub>12</sub> , 1:1, -20°, 2 hr <i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-C <sub>5</sub> H <sub>12</sub> , 1:1, 20°, 2 hr	CH <sub>3</sub> CO <sub>2</sub> H CH <sub>3</sub> I	A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOSi(CH <sub>3</sub> ) <sub>3</sub> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOH A: 90, B: 10 (-) A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(CH <sub>3</sub> )OSi(CH <sub>3</sub> ) <sub>3</sub> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOCH <sub>3</sub> + C, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOSi(CH <sub>3</sub> ) <sub>3</sub> A: 75, B: 12, C: 13 (-)	128 128
	C <sub>6</sub> H <sub>5</sub> C≡CCH(OC <sub>2</sub> H <sub>5</sub> )C <sub>3</sub> H <sub>11-n</sub> 	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> CH <sub>3</sub> Li, THF, -70°	— H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH=C=C(OC <sub>2</sub> H <sub>5</sub> )C <sub>3</sub> H <sub>11-n</sub> (-)  (95) HO C(CH <sub>3</sub> )=C=CH <sub>2</sub>	509 209
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 2 hr	—	 (84.5) HO CH(CH <sub>3</sub> )CH=CH <sub>2</sub> +  (10) O	213
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> ONa, <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH, 120°, 2 hr NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 2 hr	— —	 (-) HO CH <sub>2</sub> CH=CHCH <sub>3</sub>  (70) HO CH <sub>2</sub> CH=CHCH <sub>3</sub> +  (10-20) O	362 213

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TABLE X. ETHERS (Continued)

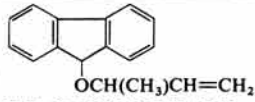
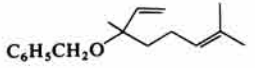
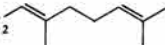
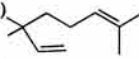

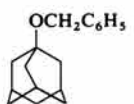

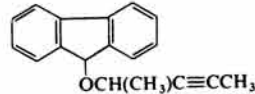
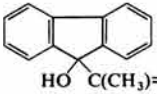
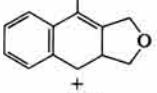
No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>17</sub> (Contd.) 	<i>n</i> -C <sub>4</sub> H <sub>9</sub> ONa, <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH, 120°, 2 hr	—	(—)	362	
	C <sub>6</sub> H <sub>5</sub> C≡CCH(OC <sub>2</sub> H <sub>5</sub> )C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OC <sub>6</sub> H <sub>4</sub> (C <sub>4</sub> H <sub>9</sub> - <i>t</i> )- <i>m</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, room temperature, 48 hr C <sub>6</sub> H <sub>5</sub> Li, THF, 0°, then 25°, 24 hr	— H <sub>2</sub> O H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH=C=C(OC <sub>2</sub> H <sub>5</sub> )C <sub>6</sub> H <sub>5</sub> (—) C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>6</sub> H <sub>4</sub> (C <sub>4</sub> H <sub>9</sub> - <i>t</i> )- <i>m</i> (—) C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>6</sub> H <sub>4</sub> (C <sub>4</sub> H <sub>9</sub> - <i>t</i> )- <i>m</i> (95) + C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub>	518 201 201
154	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OC <sub>6</sub> H <sub>4</sub> (C <sub>4</sub> H <sub>9</sub> - <i>t</i> )- <i>p</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, room temperature, 48 hr C <sub>6</sub> H <sub>5</sub> Li, THF, 0°, then 25°, 24 hr	H <sub>2</sub> O H <sub>2</sub> O	<i>t</i> -C <sub>4</sub> H <sub>9</sub> C <sub>6</sub> H <sub>4</sub> OH- <i>p</i> (5) C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>6</sub> H <sub>4</sub> (C <sub>4</sub> H <sub>9</sub> - <i>t</i> )- <i>p</i> (—) C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>6</sub> H <sub>4</sub> (C <sub>4</sub> H <sub>9</sub> - <i>t</i> )- <i>p</i> (95) + C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub>	201 201
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OC(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	H <sub>2</sub> O	<i>t</i> -C <sub>4</sub> H <sub>9</sub> C <sub>6</sub> H <sub>4</sub> OH- <i>p</i> (5) A, C <sub>6</sub> H <sub>5</sub> CH(OH)C(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )C <sub>6</sub> H <sub>5</sub> + B, C <sub>6</sub> H <sub>5</sub> C <sub>4</sub> H <sub>9</sub> - <i>sec</i> + C, C <sub>6</sub> H <sub>5</sub> CHO + D, CH <sub>3</sub> CH=C(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> + E, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH + F, C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>n</i>	
	room temperature, 12 hr -60°, 14 hr -30°, 4 hr		A: 48, B: 0.5, C: 5.5, D: 2.5, E: 2.5, F: 0.5 (—) A: (34), E: (4), F: (0.7) A: 42, B: 0.5, C: 2.5, D: 1.5, E: 1.6, F: 0.6 (—)	200 200 200	
	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> , 300 hr	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH(OH)C(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )C <sub>6</sub> H <sub>5</sub> (10) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH (1.7) + C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H (—)	200	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> -  + B, C <sub>6</sub> H <sub>5</sub> CH(OH)-  + C,  C <sub>5</sub> H <sub>11</sub> - <i>n</i> + D, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	210
	A: 45, B: 5, C: 25, D: 25 (—)		CH(OH)C <sub>6</sub> H <sub>5</sub>		
155		CH <sub>3</sub> Li (2 eq), THF, 25°, 48 hr	NH <sub>4</sub> Cl	 (54)	487
	C <sub>18</sub> 	CH <sub>3</sub> Li, THF, -70°	H <sub>2</sub> O	(95)	209
	C <sub>6</sub> H <sub>5</sub> C≡CCH <sub>2</sub> OCH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub> <i>trans</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, 55°, 16 hr	—	 (52) +  (30)	342

TABLE X. ETHERS (Continued)

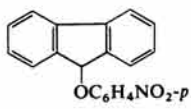
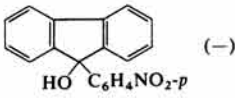
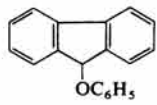
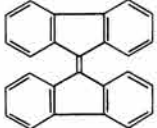

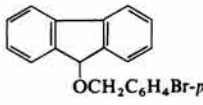
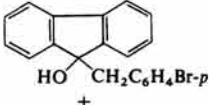
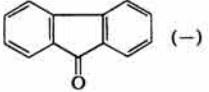
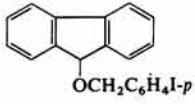
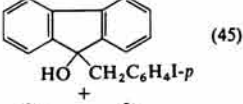
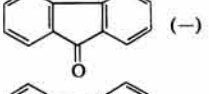
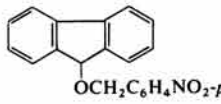
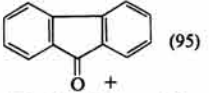
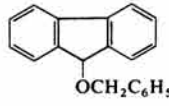
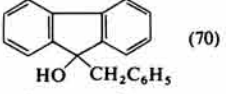
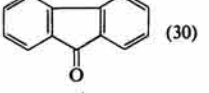
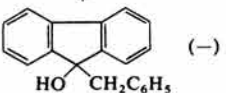
No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>19</sub>	 OC <sub>6</sub> H <sub>4</sub> NO <sub>2-p</sub>	C <sub>6</sub> H <sub>5</sub> Li, 100°, 10 hr	—	 (—)	603
	 OC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> Li, 100°, 4 hr	—	 (67)	
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOC <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, 40°, 50 hr	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> COH (85) + C <sub>6</sub> H <sub>5</sub> OH (—)	605
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , 40°, 10 days	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> COH (84)	605
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> Li, ether, room temperature, 8 days	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> COH (80) + C <sub>6</sub> H <sub>5</sub> OH (89)	605
		C <sub>6</sub> H <sub>5</sub> Li, THF, 40°, 80 hr	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> COH (78)	605
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> Li, CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , 40°, 10 days	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> COH (80)	605
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, petroleum ether, 70°, 60 hr	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> OH (56) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (38)	605
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOC <sub>6</sub> H <sub>5</sub>	KNH <sub>2</sub> , ether, NH <sub>3</sub> , 100°, 14 hr	—	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOC <sub>6</sub> H <sub>5</sub> (87)	197
		 NK, piperidine, 100°, 50 hr	—	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOC <sub>6</sub> H <sub>5</sub> (97)	197
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOC <sub>6</sub> H <sub>5</sub>	NaNH <sub>2</sub> , ether, NH <sub>3</sub> , 100°, 14 hr	—	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOC <sub>6</sub> H <sub>5</sub> (72)	197	
	LiNH <sub>2</sub> , ether, NH <sub>3</sub> , 100°, 14 hr	—	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOC <sub>6</sub> H <sub>5</sub> (76)	197	
C <sub>20</sub>	 OCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br- <i>p</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> ONa, <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH, 120°, 2.5 hr	—	 (61) +  (—)	362
	 OCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> I- <i>p</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> ONa, <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH, 120°, 2.5 hr	—	 (45) +  (—)	362
	 OCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2-p</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> ONa, <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH, 75°, 3 hr	—	 (95) + CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2-p</sub> (55)	362
	 OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> ONa, <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH, 120°, 2.5 hr	—	 (70)	362
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOC <sub>6</sub> H <sub>5</sub>	KNH <sub>2</sub> , NH <sub>3</sub> (liq), ether, -30° to 10°, 1 hr	—	 (30) +  (—)	362

TABLE X. ETHERS (Continued)

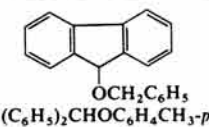
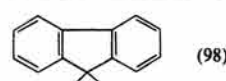
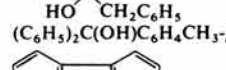
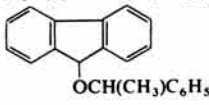
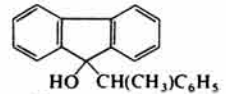
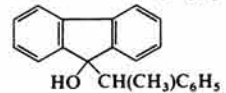
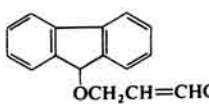
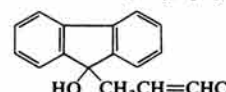
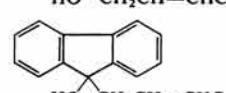
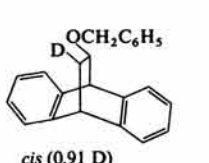
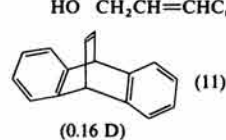
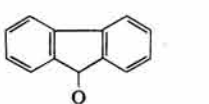
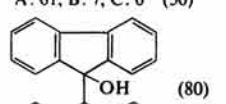
No. of C Atoms Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>20</sub> (Contd.) 	C <sub>6</sub> H <sub>5</sub> Li (1.1 eq), ether, -10°	H <sub>2</sub> O	 (98)	603
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	KNH <sub>2</sub> , ether, NH <sub>3</sub> , 100°, 17 hr	—	 (77)
C <sub>21</sub> 	<i>n</i> -C <sub>4</sub> H <sub>9</sub> ONa, <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH, 110°, 2 hr	—	 (80)	362
	C <sub>6</sub> H <sub>5</sub> Li, ether, 15°, 4 min	H <sub>2</sub> O	 (60)	362
C <sub>22</sub> 	C <sub>6</sub> H <sub>5</sub> Li, ether, 15°, 1 min	H <sub>2</sub> O	 (90)	362
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> ONa, <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH, 120°, 120°, 20 hr	—	 (70)	362
C <sub>23</sub>  <i>cis</i> (0.91 D)	CH <sub>3</sub> Li, THF, -70° then 0°, 23 hr	H <sub>2</sub> O	 (11) (0.16 D)	177
C <sub>25</sub> C <sub>6</sub> H <sub>5</sub> CHDOGe(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li (eq), THF- <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 1:1, -50°, 3 min	CH <sub>3</sub> CO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> CD(OH)Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> S(-): 53, R(+): 47 (-)	493
	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-C <sub>5</sub> H <sub>12</sub> , 1:1, -40°, 18 hr	CH <sub>3</sub> CO <sub>2</sub> H	A, C <sub>6</sub> H <sub>5</sub> CH(OH)Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH + C, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> A: 61, B: 7, C: 6 (50)	128
C <sub>26</sub>  [(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH] <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> Li (1 eq), ether	H <sub>2</sub> O	 (80)	603
	CH <sub>3</sub> Li (5 eq), THF, 25°, 48 hr	NH <sub>4</sub> Cl	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (3) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (-) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH)CH <sub>3</sub> (12) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHOH (32) [ <i>o</i> -HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> O] (-) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCOOH (60-68) + C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (15-20) + C <sub>6</sub> H <sub>5</sub> CONH <sub>2</sub> (-) C <sub>6</sub> H <sub>5</sub> COC(OH)(C <sub>6</sub> H <sub>5</sub> )CH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (5)	487
C <sub>27</sub> C <sub>6</sub> H <sub>5</sub> COCH(C <sub>6</sub> H <sub>5</sub> )OCH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, 48 hr KNH <sub>2</sub> (2 eq), ether, room temperature, then reflux 3.5 hr	CO <sub>2</sub> CO <sub>2</sub>		384 208
C <sub>30</sub> [C <sub>6</sub> H <sub>5</sub> CH=CHCH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ]O	KOH, <i>N</i> , C <sub>2</sub> H <sub>5</sub> OH, reflux, 1 hr	—		444
	C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH, reflux 2 hr	—	[C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH=C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ]O (-)	578

TABLE XI. HEMITHIOKETALS

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>9</sub>		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NLi, ether, 20°, 15 min	—	C <sub>6</sub> H <sub>5</sub> CON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (—)	31
		LICA, ether, 20°, 15 min	—	C <sub>6</sub> H <sub>5</sub> CON(C <sub>3</sub> H <sub>7-i</sub> ) (—)	31
C <sub>13</sub>		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NLi, ether	—	(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub> (—)	31
C <sub>15</sub>		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NLi, ether, 20°, 12 hr	—	(45)	31
		LICA, ether, 20°, 15 min	—	(29)	31
C <sub>21</sub>		LICA, ether, 20°, 2 d	—	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> <i>cis</i> (—)	31

TABLE XII. IMINODITHIOLCARBONATE DIESTERS



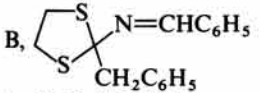
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>10</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -70°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	A,  + B, 	24	
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N=C(SCH <sub>3</sub> ) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> I	A: 15, B: 85 (80) A, C <sub>6</sub> H <sub>5</sub> CHRN=C(SCH <sub>3</sub> ) <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> CH=NC(SCH <sub>3</sub> ) <sub>2</sub> R	24
			LDA, THF, -78°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (CH <sub>3</sub> ) <sub>3</sub> SiCl	A: 40, B: 60, R = C <sub>2</sub> H <sub>5</sub> (95) A: 90, B: 10, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (81) A: 15, B: 85, R = Si(CH <sub>3</sub> ) <sub>3</sub> (80)	24 24 24

TABLE XIII. ISONITRILES


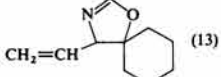
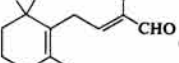
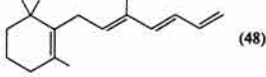
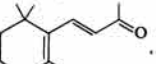
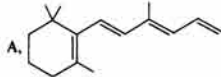
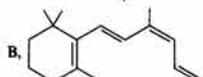
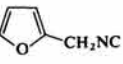

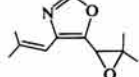
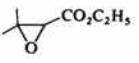
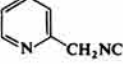
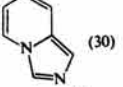
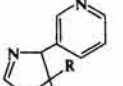
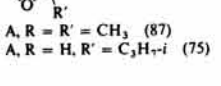

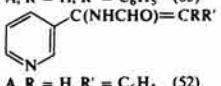
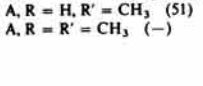

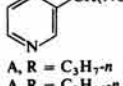
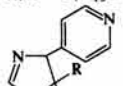

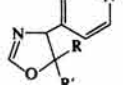
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.		
C <sub>4</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> NC	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	C <sub>6</sub> H <sub>5</sub> CHO, 65°	CH <sub>2</sub> =CHCH=CHC <sub>6</sub> H <sub>5</sub> (41)	245,317		
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> , -70°	CH <sub>2</sub> =CHCH=C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (38)	245		
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> , excess	CH <sub>2</sub> =CH-N(C <sub>6</sub> H <sub>5</sub> )C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (4.6)	246		
				 (13)	246		
				 (48)	245		
			reflux, 16 hr				
				A, 	245		
			reflux, 16 hr	B, 			
				A: 2, B: 1 (25)			
				C <sub>6</sub> H <sub>5</sub> CH=CHCH=CH <sub>2</sub> (53.5)	245		
C <sub>6</sub>		NaH, THF, reflux, 2 hr	C <sub>6</sub> H <sub>5</sub> CHO, room temperature, 16 hr	 (61)	152		
			NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO	C <sub>2</sub> H <sub>5</sub> OCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	 (50)	256	
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70° to -60°				
C <sub>7</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -70° to -60°	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, 52°	 (30)	146		
			—	 (87)	566		
			CH <sub>3</sub> COCH <sub>3</sub> , then CH <sub>3</sub> OH	 (75)	566		
			<i>i</i> -C <sub>3</sub> H <sub>7</sub> CHO, then CH <sub>3</sub> OH	A, R = R' = (CH <sub>2</sub> ) <sub>5</sub> (72)	566		
				A, R = H, R' = C <sub>6</sub> H <sub>5</sub> (65)	566		
			C <sub>6</sub> H <sub>5</sub> CHO, then CH <sub>3</sub> OH	 (65)	146		
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF, -60°	C <sub>6</sub> H <sub>5</sub> CHO, room temperature, then reflux, 45 min, then H <sup>+</sup>	 (52)	146	
			CH <sub>3</sub> CHO	A, R = H, R' = CH <sub>3</sub> (51)	146		
			CH <sub>3</sub> COCH <sub>3</sub>	A, R = R' = CH <sub>3</sub> (-)	146		
				A, R = R' = (CH <sub>2</sub> ) <sub>5</sub> (92)	146		
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	A, R = R' = C <sub>6</sub> H <sub>5</sub> (75)	146		
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq), THF, -60°	<i>n</i> -C <sub>3</sub> H <sub>7</sub> I, warmed to room temperature	 (60)	146	
			<i>n</i> -C <sub>7</sub> H <sub>15</sub> Br	 (53)	146		
				<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -70° to -65°	CH <sub>3</sub> CHO, then CH <sub>3</sub> OH	 (65)	566
					CH <sub>3</sub> COCH <sub>3</sub> , then CH <sub>3</sub> OH	A, R = H, R' = CH <sub>3</sub> (-)	566
	A, R = R' = CH <sub>3</sub> (65)	566					

TABLE XIII. ISONITRILES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>7</sub> (Contd.)		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -70° to -65°	then CH <sub>3</sub> OH	A, R = R' = (CH <sub>2</sub> ) <sub>4</sub> (73)	566
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF, <10°	CH <sub>3</sub> CHO C <sub>6</sub> H <sub>5</sub> CHO, room temperature, then H <sup>+</sup> CH <sub>3</sub> COCH <sub>3</sub>	 C(NHCHO)=CRR' A, R = H, R' = CH <sub>3</sub> (73) A, R = H, R' = C <sub>6</sub> H <sub>5</sub> (90) A, R = R' = CH <sub>3</sub> (94)	146 146 146
164	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NC	NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO		A, R = R' = (CH <sub>2</sub> ) <sub>4</sub> (90)	146
			CH <sub>3</sub> COC <sub>6</sub> H <sub>5</sub> - <i>f</i> C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub> OCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	A, R = CH <sub>3</sub> , R' = C <sub>6</sub> H <sub>5</sub> - <i>f</i> (95) A, R = R' = C <sub>6</sub> H <sub>5</sub> (>90) <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH(NC)CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (62)	146 146 152
C <sub>8</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NC	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70° to -65°	CH <sub>2</sub> O, then CH <sub>3</sub> OH	 A, R = R' = H (-) A, R = H, R' = C <sub>6</sub> H <sub>5</sub> (64) A, R = CH <sub>3</sub> , R' = C <sub>6</sub> H <sub>5</sub> (46) A, R = H, R' = C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub> - <i>p</i> (62)	566 566 566 566
			C <sub>6</sub> H <sub>5</sub> CHO, then CH <sub>3</sub> OH C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> , then CH <sub>3</sub> OH <i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO, then CH <sub>3</sub> OH	HCO <sub>2</sub> CH <sub>3</sub> , -50° to room temperature	 (76)
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NC	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70° to -60°	<i>i</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> CH <sub>3</sub>	 (44)	256
			<i>i</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -70° to -60°	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO, then CH <sub>3</sub> OH	 (48)
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NC	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	C <sub>6</sub> H <sub>5</sub> CHCHCOCl	 (-)	317
			CS <sub>2</sub> , then CH <sub>3</sub> I	 A, R = SCH <sub>3</sub> (-) A, R = NHC <sub>6</sub> H <sub>5</sub> (24) A, R = N(CH <sub>3</sub> )CSNCH <sub>3</sub> (11)	317 317 317
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NC	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	CH <sub>3</sub> CH=CHCH <sub>2</sub> Br	CH <sub>3</sub> CH=CHCH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )NC (89)	317
				 (89)	317
165	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NC	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°		 (26)	246
			C <sub>6</sub> H <sub>5</sub> CHO, then heat	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (-)	317
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NC	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> , 65°	<i>cis</i> C <sub>6</sub> H <sub>5</sub> CH=C(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (44)	21
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> , -70°	<i>trans</i> C <sub>6</sub> H <sub>5</sub> CH=C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (74)	21
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NC	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> , excess	 C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (16)	246
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NC	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	CO <sub>2</sub> , then HCl ClCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> CH <sub>3</sub> OCO <sub>2</sub> CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH(NH <sub>2</sub> )CO <sub>2</sub> H (40) C <sub>6</sub> H <sub>5</sub> CH(NC)CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (35) C <sub>6</sub> H <sub>5</sub> CH(CO <sub>2</sub> CH <sub>3</sub> )NC (70)	152 152 152



TABLE XIII. ISONITRILES (Continued)

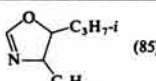
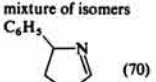
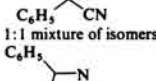
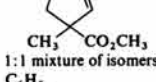
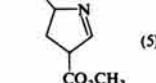
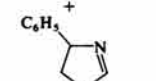
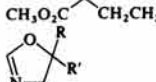
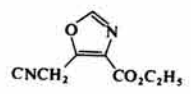

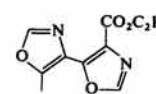
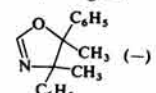
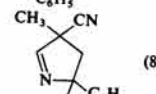
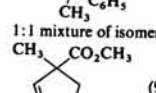
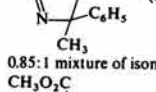
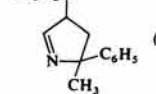
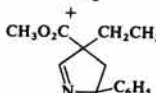
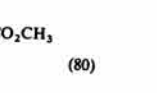
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>8</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NC	Cu <sub>2</sub> O (2 eq), C <sub>6</sub> H <sub>6</sub> , 80°, 1 hr	<i>i</i> -C <sub>3</sub> H <sub>7</sub> CHO (2 eq)	 (85)	559	
			CH <sub>2</sub> =C(CH <sub>3</sub> )CN (1 eq)	mixture of isomers  (70)	559	
			CH <sub>2</sub> =C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub> (1 eq)	1:1 mixture of isomers  (94)	559	
			CH <sub>2</sub> =CHCO <sub>2</sub> CH <sub>3</sub> (2 eq)	1:1 mixture of isomers  (5)	559	
			CH <sub>3</sub> COCH <sub>3</sub> (2 eq)	 (75)	559	
			C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> (2 eq)	 (60)  (75) mixture of isomers	559 559	
C <sub>9</sub>		Cu <sub>2</sub> O (2 eq), C <sub>6</sub> H <sub>6</sub> , 80°, 15 hr	 (2 eq)	A, R = R' = (CH <sub>2</sub> ) <sub>4</sub> (82)	559	
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -55°, 20 min	CH <sub>3</sub> COCl	 (31)	154a
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> , then CH <sub>3</sub> OH	 (-)	317, 566
C <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )NC	Cu <sub>2</sub> O (2 eq), C <sub>6</sub> H <sub>6</sub> , 80°, 3 hr	CH <sub>2</sub> =C(CH <sub>3</sub> )CN (1 eq)	 (85)	559	
			CH <sub>2</sub> =C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub> (1 eq)	1:1 mixture of isomers  (95)	559	
			CH <sub>2</sub> =CHCO <sub>2</sub> CH <sub>3</sub> (2 eq)	0.85:1 mixture of isomers  (2-3)	559	
			CH <sub>3</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (1 eq)	 (80)  (40) +  (20)	559	

TABLE XIII. ISONITRILES (Continued)

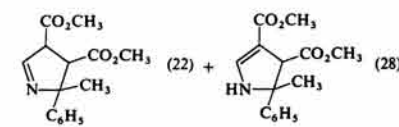
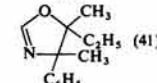
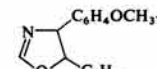
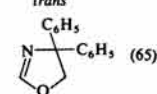

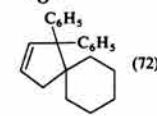
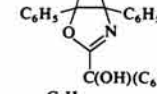
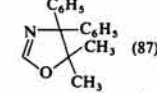
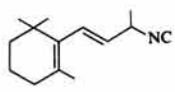
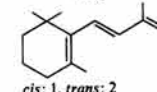
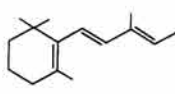
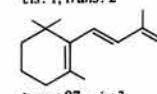
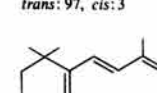
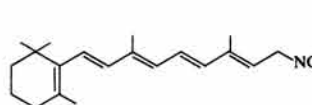
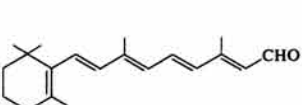
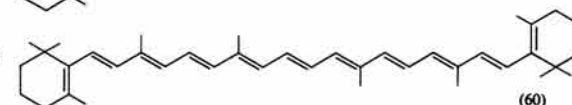
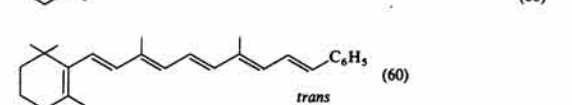
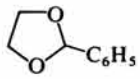
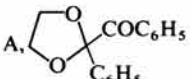
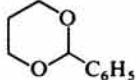
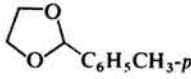
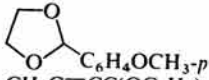
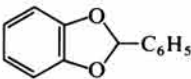
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>9</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )NC	Cu <sub>2</sub> O (2 eq), C <sub>6</sub> H <sub>6</sub> , 80°, 3 hr	CH <sub>3</sub> O <sub>2</sub> CCH=CHCO <sub>2</sub> CH <sub>3</sub> (2 eq)	 (22) + (28)	559
168		Cu <sub>2</sub> O (2 eq), C <sub>6</sub> H <sub>6</sub> , 80°, 15 hr	CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub> (2 eq)	 (41)	559
	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NC	NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO	C <sub>2</sub> H <sub>5</sub> OCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	mixture of isomers <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH(NC)CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (59)	152
	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NC	NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO	C <sub>2</sub> H <sub>5</sub> OCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH(NC)CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (60)	152
C <sub>10</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70° to -65°	C <sub>6</sub> H <sub>5</sub> CHO, then CH <sub>3</sub> OH	 (78)	566
	C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> NC <i>trans</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	C <sub>6</sub> H <sub>5</sub> CHO, reflux 16 hr	C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHC <sub>6</sub> H <sub>5</sub> (53) <i>trans</i>	245
C <sub>14</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHNC	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70° to -65°	CH <sub>2</sub> O, then CH <sub>3</sub> OH	 (65)	566
			 , then CH <sub>3</sub> OH	 (72)	246, 566
			C <sub>6</sub> H <sub>5</sub> CHO, then heat	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHC <sub>6</sub> H <sub>5</sub> (-)	317
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> , excess	 (95)	246
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -70° to -60°	CH <sub>3</sub> COCH <sub>3</sub> , then CH <sub>3</sub> OH	 (87)	566
C <sub>16</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 5 min	C <sub>6</sub> H <sub>5</sub> CHO, reflux, 16 hr	 (30)	245
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 10 min	C <sub>6</sub> H <sub>5</sub> CHO, reflux 16 hr	 (36)	245
			CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> )CHO, reflux	 (27)	245
C <sub>21</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 10 min	 CHO room temperature, 4 hr	 (60)	245
			C <sub>6</sub> H <sub>5</sub> CHO, reflux, 16 hr	 (60) <i>trans</i>	246

TABLE XIV. KETALS

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub>	CH <sub>3</sub> C≡CCH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	NaNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq)	H <sub>2</sub> O	HC≡CCH=CHOC <sub>2</sub> H <sub>5</sub> (80)	183
C <sub>9</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> CH <sub>2</sub> Li, ether	—	A,  + B, C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i> A: 8, B: 92 (—)	191
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>14</sub> , 60°, 30 min	—	C <sub>6</sub> H <sub>5</sub> COC <sub>4</sub> H <sub>9</sub> - <i>n</i> (87)	345
		<i>n</i> -C <sub>6</sub> H <sub>13</sub> Li, C <sub>6</sub> H <sub>14</sub> , 60°, 30 min	—	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>13</sub> - <i>n</i> (66)	345
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -5°, 10 min	NH <sub>4</sub> Cl	C <sub>6</sub> H <sub>5</sub> CHO + C <sub>6</sub> H <sub>5</sub> COC <sub>4</sub> H <sub>9</sub> - <i>n</i> (—)	589
		C <sub>6</sub> H <sub>5</sub> Li (1.25 eq), ether, room temperature	H <sub>2</sub> O	C <sub>2</sub> H <sub>4</sub> (—) + C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (—) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> COH (—)	601
C <sub>10</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	—	C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>n</i> (17) +	191
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.2 eq), THF, 20°, 2 hr	—	<i>n</i> -C <sub>5</sub> H <sub>11</sub> C(OH)(C <sub>6</sub> H <sub>5</sub> )(CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH (30) C <sub>6</sub> H <sub>5</sub> C(OH)(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )(CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH (—) +	192
				C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>n</i> (—)	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>12</sub> , 60°, 30 min	—	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COC <sub>4</sub> H <sub>9</sub> - <i>n</i> (80)	345
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>6</sub> H <sub>12</sub> , 60°, 30 min	—	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COC <sub>4</sub> H <sub>9</sub> - <i>n</i> (78)	345
	CH <sub>3</sub> C≡CC(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	KNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq)	H <sub>2</sub> O	HC≡CCH=C(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (75)	170, 183
	C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> C≡CCH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -40° to -50°, 35 min	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> OCH=C=C=CHOC <sub>2</sub> H <sub>5</sub> (60)	170, 183
C <sub>11</sub>	C <sub>6</sub> H <sub>5</sub> CH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	—	C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>n</i> (50) +	191
				C <sub>6</sub> H <sub>5</sub> CHO (20) + C <sub>6</sub> H <sub>5</sub> COC <sub>2</sub> H <sub>5</sub> (15) +	
				C <sub>2</sub> H <sub>5</sub> C(OH)(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub> - <i>n</i> (5) C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>n</i> + C <sub>6</sub> H <sub>5</sub> CHO (—) +	192
				C <sub>6</sub> H <sub>5</sub> COC <sub>2</sub> H <sub>5</sub> (—) +	
				C <sub>6</sub> H <sub>5</sub> C(OH)(C <sub>2</sub> H <sub>5</sub> )C <sub>4</sub> H <sub>9</sub> - <i>n</i> (—) C <sub>2</sub> H <sub>5</sub> OC(CH <sub>3</sub> )=C=C=CHOC <sub>2</sub> H <sub>5</sub> +	170
				CH <sub>3</sub> CH=C=C=C(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (83, total)	
C <sub>12</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CHC≡CCH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , room temperature	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CHCH=C=CHOC <sub>4</sub> H <sub>9</sub> - <i>t</i> (70)	34
C <sub>13</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, petroleum ether, 20°, 38 hr	—	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub> -1,2 (—) +	106
				C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>3</sub> H <sub>7</sub> - <i>n</i> (—) <i>cis</i> and <i>trans</i> +	
				C <sub>6</sub> H <sub>5</sub> CH(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )OC <sub>6</sub> H <sub>4</sub> OH- <i>o</i> (30) C <sub>6</sub> H <sub>5</sub> CH=C=C(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (—)	34
	C <sub>6</sub> H <sub>5</sub> C≡CCH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , room temperature	—		

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TABLE XIV. KETALS (Continued)

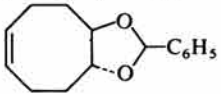
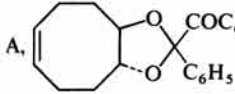
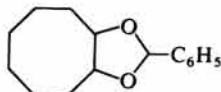
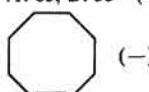
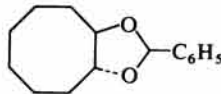
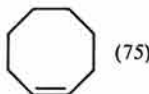
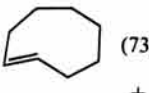

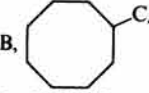
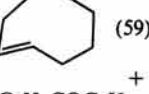
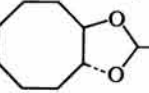
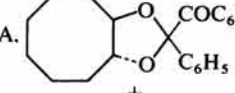
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>13</sub> (Contd.)	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CHC≡CCH(CH <sub>3</sub> )OC <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , 45°, 2 hr	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CHCH=C=C(CH <sub>3</sub> )OC <sub>4</sub> H <sub>9</sub> - <i>t</i> (70)	34
C <sub>14</sub>	C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> C≡CCH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , room temperature	—	C <sub>6</sub> H <sub>5</sub> OCH=C=CHCH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (20)	34
C <sub>15</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OCH <sub>3</sub> ) <sub>2</sub>	K (2 eq)	CO <sub>2</sub> , H <sup>+</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OCH <sub>3</sub> )CO <sub>2</sub> H (—)	93
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> CH <sub>2</sub> Li, ether, 20°, 15 hr	—	A,  + B, C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i> A: 65, B: 35 (—)	192
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), C <sub>6</sub> H <sub>14</sub> , 20°, 12 hr	—	 (—) <i>cis</i>	192
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, petroleum ether	—	 (75) <i>trans</i> + C <sub>6</sub> H <sub>5</sub> COC <sub>4</sub> H <sub>9</sub> - <i>n</i> (—)	191
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), petroleum ether, 20°, 14 hr	—	 (73) + C <sub>6</sub> H <sub>5</sub> COC <sub>4</sub> H <sub>9</sub> - <i>n</i> (5)	192
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, 0°, 15 min	—	A,  + B,  -C <sub>4</sub> H <sub>9</sub> - <i>n</i> A: 82, B: 18 A: 62, B: 38	192 192
		0°, 1 hr	—	 (59) + C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (—) +	192
		C <sub>6</sub> H <sub>5</sub> Li, THF, reflux, 2 hr	—	 (—) +	192
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> CH <sub>2</sub> Li, ether	—	A,  + B, C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i> A: 30, B: 70 (—)	192

TABLE XIV. KETALS (Continued)

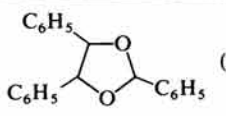
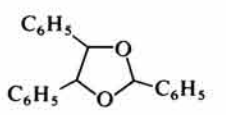
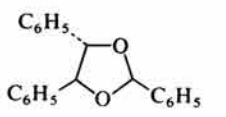
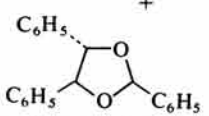
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>21</sub>	 (±)	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	—	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (9) <i>trans</i> + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (66) + C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>n</i> (64) C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (67)	191
	<i>meso</i> , mixture of diastereomers	—	—	+ C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>n</i> (70)	191
	 (±)	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.1 eq), THF, 20°, 2 hr	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (—) + C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>n</i> (—)	192
	 (±)	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.1 eq), THF, 20°, 1.5 hr	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (9) <i>trans</i> + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (—) + C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>n</i> (—) +  (—)	192

TABLE XV. NITRO DERIVATIVES

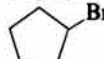


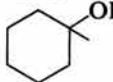
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>3</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> NO <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -80° to -90°	D <sub>2</sub> O	A, CH <sub>2</sub> =CHCHRCH <sub>2</sub> NO <sub>2</sub> + B, RCH <sub>2</sub> CH=CHCH <sub>2</sub> NO <sub>2</sub> A: 52, B: 48, R = D (80) A: 40, B: 60, R = CH <sub>3</sub> (71) A: 12, B: 88, R = C <sub>8</sub> H <sub>17</sub> - <i>n</i> (75) A: 3, B: 97, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (53)	619 619 619 619
			CH <sub>3</sub> I	A: 20, B: 80, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (53)	619
			<i>n</i> -C <sub>8</sub> H <sub>17</sub> I	A: 20, B: 80, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (53)	619
			<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	A: 20, B: 80, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (53)	619
				A: 20, B: 80, R =  (68)	619
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	A: 20, B: 80, R = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (68)	619
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> CHO	A: 52, B: 48, R = <i>t</i> -C <sub>4</sub> H <sub>9</sub> CH(OH) (65)	619
			<i>n</i> -C <sub>5</sub> H <sub>11</sub> CHO	A: 56, B: 44, R = <i>n</i> -C <sub>5</sub> H <sub>11</sub> CH(OH) (76)	619
			C <sub>6</sub> H <sub>5</sub> CHO	A: 30, B: 70, R = C <sub>6</sub> H <sub>5</sub> CH(OH) (74)	619
				A: 50, B: 50, R =  (82)	619
C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	A: 50, B: 50, R = (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH) (42)	619			

TABLE XV. NITRO DERIVATIVES (Continued)

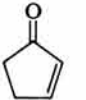
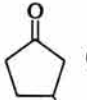
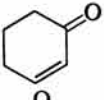
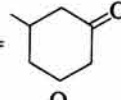

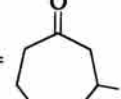
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>3</sub> (Contd.)	CH <sub>2</sub> =CHCH <sub>2</sub> NO <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -80° to -90°		A: 0, B: 100, R =  (40)	619
				A: 0, B: 100, R =  (48)	619
				A: 0, B: 100, R =  (68)	619
C <sub>7</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NO <sub>2</sub>	LDA, THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 5:1, -78°, 1 hr	C <sub>6</sub> H <sub>5</sub> COCH=CHC <sub>6</sub> H <sub>5</sub> , C <sub>2</sub> H <sub>5</sub> I	A: 0, B: 100, R = C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> ) (-)	619
			<i>n</i> -C <sub>5</sub> H <sub>11</sub> Br	C <sub>6</sub> H <sub>5</sub> CH(R)NO <sub>2</sub> A, R = C <sub>2</sub> H <sub>5</sub> (80)	29a
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	A, R = C <sub>5</sub> H <sub>11</sub> - <i>n</i> (80)	29a
			Br(CH <sub>2</sub> ) <sub>5</sub> Br	A, R = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (75) A, R = (CH <sub>2</sub> ) <sub>5</sub> Br (40)	29a 29a

TABLE XVI. NITROSOAMINES


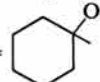
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>4</sub>	CH <sub>3</sub> N(NO)CH <sub>2</sub> CH=CH <sub>2</sub>	LDA, THF, -78°	CH <sub>3</sub> I, -30°, 8 hr	CH <sub>3</sub> N(NO)CH(R)CH=CH <sub>2</sub> A, R = CH <sub>3</sub> (87)	620
			 , -30°, 2 hr	A, R =  (92)	620
			C <sub>6</sub> H <sub>5</sub> CHO, -78°, 35 min	A, R = C <sub>6</sub> H <sub>5</sub> CH(OH) (90)	620
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> , -78°	A, R = C <sub>6</sub> H <sub>5</sub> C(OH)C <sub>6</sub> H <sub>5</sub> (80)	620
			-78°, 12 hr	CH <sub>3</sub> N(NO)CH=CHCH <sub>2</sub> C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (76)	620
C <sub>7</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> N(NO)C <sub>4</sub> H <sub>9</sub> - <i>t</i>	LDA, THF,	C <sub>6</sub> H <sub>5</sub> CHO	A, CH <sub>2</sub> =CHCH[CH(OH)(C <sub>6</sub> H <sub>5</sub> )]N(NO)C <sub>4</sub> H <sub>9</sub> - <i>t</i>	
		-80°, 5 min		+ B, C <sub>6</sub> H <sub>5</sub> CH(OH)CH <sub>2</sub> CH=CHN(NO)C <sub>4</sub> H <sub>9</sub> - <i>t</i>	4, 575
		-80° to -30°, 2 hr		A: 55, B: 45 (-)	4, 575
		-80° to +25°, 12 hr		A: 45, B: 55 (-)	4, 575
		LDA, THF, -80°	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> N(NO)CH=CHCH <sub>2</sub> C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (-)	10
		LDA, THF, -78°, 3 min	CH <sub>3</sub> I, -30°, 8 hr	<i>t</i> -C <sub>4</sub> H <sub>9</sub> N(NO)CH(R)CH=CH <sub>2</sub> A, R = CH <sub>3</sub> (80)	620
			<i>n</i> -C <sub>8</sub> H <sub>17</sub> I	A, R = <i>n</i> -C <sub>8</sub> H <sub>17</sub> (75)	620
			<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	A, R = <i>i</i> -C <sub>3</sub> H <sub>7</sub> (40)	620
			CH <sub>2</sub> =CHCH <sub>2</sub> Br	A, R = CH <sub>2</sub> =CHCH <sub>2</sub> (85)	620
			C <sub>2</sub> H <sub>5</sub> CHO, -30°, 2 hr	A, <i>t</i> -C <sub>4</sub> H <sub>9</sub> N(NO)CH(R)CH=CH <sub>2</sub>	
				+ B, <i>t</i> -C <sub>4</sub> H <sub>9</sub> N(NO)CH=CHCH <sub>2</sub> R	
			CH <sub>3</sub> COCH <sub>3</sub>	A: 98, B: 2, R = C <sub>2</sub> H <sub>5</sub> CH(OH) (95)	620
				A: 45, B: 55, R = (CH <sub>3</sub> ) <sub>2</sub> C(OH) (95)	620



TABLE XVI. NITROSOAMINES (Continued)


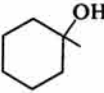

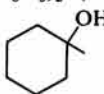
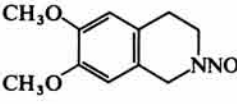
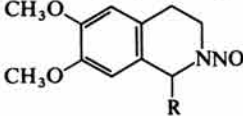
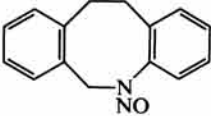
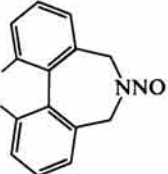
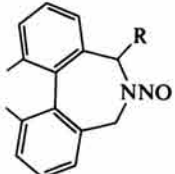
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>7</sub> (Contd.)	CH <sub>2</sub> =CHCH <sub>2</sub> N(NO)C <sub>4</sub> H <sub>9</sub> - <i>t</i>	LDA, THF, -78°, 3 min		A: 40, B: 60, R =  (85)	620	
			C <sub>6</sub> H <sub>5</sub> CHO C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	A: 45, B: 55, R = C <sub>6</sub> H <sub>5</sub> CH(OH) (>95) A: 2, B: 98, R = (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH) (>95)	620 620	
				A, 0, B: 100, R =  (76)	620	
			room temperature C <sub>6</sub> H <sub>5</sub> CHO, room temperature	A: 5, B: 95, R = C <sub>6</sub> H <sub>5</sub> CH(OH) (78)	620	
C <sub>8</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(NO)CH <sub>3</sub>	LDA, THF, -78°, 10 min	CH <sub>3</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(NO)[CH <sub>2</sub> CH(OH)CH <sub>3</sub> ] + C <sub>6</sub> H <sub>5</sub> CH[CH(OH)CH <sub>3</sub> ]N(NO)CH <sub>3</sub> (100)	23	
C <sub>11</sub>		LDA, THF, -80°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	 A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (60) A, R = CH(OH)C <sub>6</sub> H <sub>3</sub> (OCH <sub>3</sub> ) <sub>2</sub> - <i>m,p</i> (60)	10, 621	
C <sub>14</sub>	(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> NNO	LDA, THF, -78°, 4 min	<i>m,p</i> -(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO	A, R = CH(OH)C <sub>6</sub> H <sub>3</sub> (OCH <sub>3</sub> ) <sub>2</sub> - <i>m,p</i> (60)	10, 621	
			CH <sub>3</sub> I, -78°, 1.5 hr, then 0°	A, R = CH <sub>3</sub> (91) <i>anti</i> : 4, <i>syn</i> : 1	25	
			Br(CH <sub>2</sub> ) <sub>3</sub> Br, -78°, 1.5 hr, then 0°	A, R = (CH <sub>2</sub> ) <sub>3</sub> Br (-) <i>anti</i> : 9, <i>syn</i> : 1	25	
			Br(CH <sub>2</sub> ) <sub>4</sub> Br, -78°, 1.5 hr, then 0°	A, R = (CH <sub>2</sub> ) <sub>4</sub> Br (-) <i>anti</i> : 9, <i>syn</i> : 1	25	
			CO <sub>2</sub> , -78°, 20 min	A, R = CO <sub>2</sub> H (99) <i>anti</i> : 2, <i>syn</i> : 1	25	
			C <sub>6</sub> H <sub>5</sub> CHO (1 eq), -78°, 1.5 hr, then 0°	A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (66) two isomers, <i>anti</i>	25	
			CH <sub>3</sub> Li, THF, -75°, 4 min	A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (90)	25	
			LDA, THF, -80°	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (-)	10	
			LDA, THF, -75°, 4 min	<i>n</i> -C <sub>3</sub> H <sub>7</sub> I, -75°, 2.5 hr, then room temperature	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(NO)CH(C <sub>3</sub> H <sub>7</sub> - <i>n</i> )C <sub>6</sub> H <sub>5</sub> <i>anti</i> : 85, <i>syn</i> : 15 (85)	25
			C <sub>15</sub>		LDA, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO	CH <sub>3</sub> I
C <sub>16</sub>		CH <sub>3</sub> Li (1.1 eq), THF, -78°, 1 min	CH <sub>3</sub> I, 30 min		25	
			CO <sub>2</sub>	A, R = CH <sub>3</sub> (98) A, R = CO <sub>2</sub> H (45) <i>anti</i> : 1, <i>syn</i> : 2	25	
			D <sub>2</sub> O	A, R = D (-) <i>anti</i> : 2, <i>syn</i> : 9	25	
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OD, 27 min	-	A, R = D (-) H <i>syn</i> axial exchanged faster	408

TABLE XVII. PHOSPHATES


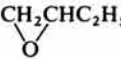
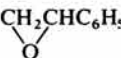
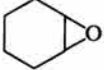
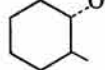



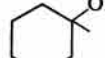

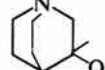


No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>7</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)OCH <sub>2</sub> CH=CH <sub>2</sub> [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)OCH <sub>2</sub> CH=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	CH <sub>3</sub> COCl	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(OCOCH <sub>3</sub> )CH=CH <sub>2</sub> (72)	206
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	H <sub>2</sub> O	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)CH(OH)CH=CH <sub>2</sub> (50)	206
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	CH <sub>3</sub> COCl	A, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)CH(OCOCH <sub>3</sub> )CH=CH <sub>2</sub> + B, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)C(OCOCH <sub>3</sub> )=CHCH <sub>3</sub> A: 1, B: 1 (70)	206
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (excess), THF, -70°	CH <sub>3</sub> COCl	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)C(OCOCH <sub>3</sub> )=CHCH <sub>3</sub> (-)	206
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (excess), THF, -70° inverse addition,	CH <sub>3</sub> I	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)COC <sub>2</sub> H <sub>4</sub> R A, R = CH <sub>3</sub> (-) not isolated	206
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	<i>n</i> -C <sub>3</sub> H <sub>7</sub> I Br(CH <sub>2</sub> ) <sub>3</sub> Br (0.5 eq)	A, R = C <sub>3</sub> H <sub>7</sub> - <i>n</i> (-) not isolated A, R = (CH <sub>2</sub> ) <sub>5</sub> COP(O)[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (-) not isolated	206 206
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, -50°, 1.5 hr	C <sub>6</sub> H <sub>5</sub> CH=CHCOCH <sub>3</sub>	A, R = C(OH)(CH <sub>3</sub> )CH=CHC <sub>6</sub> H <sub>5</sub> (-) not isolated	581
				A, R = CH <sub>2</sub> CH(OH)CH <sub>3</sub> (-) not isolated	581
				A, R = CH <sub>2</sub> CH(OH)C <sub>2</sub> H <sub>5</sub> (-) not isolated	581
				A, R = CH <sub>2</sub> CH(OH)C <sub>6</sub> H <sub>5</sub> (-) not isolated	581
				A, R =  (-) not isolated	581
			<i>n</i> -C <sub>5</sub> H <sub>11</sub> CHO	A, R = CH(OH)C <sub>5</sub> H <sub>11</sub> - <i>n</i> (-) not isolated	581
			<i>i</i> -C <sub>3</sub> H <sub>7</sub> CHO	A, R = CH(OH)C <sub>3</sub> H <sub>7</sub> - <i>i</i> (-) not isolated	206, 581
	C <sub>6</sub> H <sub>5</sub> CHO	A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (-) not isolated	581		
	CH <sub>3</sub> COCH <sub>3</sub>	A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (-) not isolated	581		
		A, R =  (-) not isolated	581		
		A, R =  (-) not isolated	581		
		A, R =  (-) not isolated	581		
		A, R =  (-) not isolated	581		
C <sub>8</sub>	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)OCH <sub>2</sub> CH=CHCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> H <sub>2</sub> O	A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (-) [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)CH(OH)CH=CHCH <sub>3</sub> (50)	581 206

TABLE XVII. PHOSPHATES (Continued)

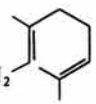
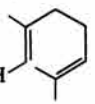
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub> (Contd.)	$[(CH_3)_2N]_2P(O)OCH_2CH=CHCH_3$	$n-C_4H_9Li$ , THF, $-70^\circ$	$CH_3COCl$	A, $[(CH_3)_2N]_2P(O)CH(OCOCH_3)CH=CHCH_3$ (48) 206 + B, $[(CH_3)_2N]_2P(O)C(OCOCH_3)=CHC_2H_5$ (32)	
C <sub>9</sub>	$(CH_3O)_2P(O)OCH_2C_6H_4Br-p$	$n-C_4H_9Li$ (1 eq), THF, $-70^\circ$	$CH_3COCl$	$(CH_3O)_2P(O)CH(OCOCH_3)C_6H_4Br-p$ (70)	36
	$(CH_3O)_2P(O)OCH_2C_6H_5$	$n-C_4H_9Li$ (1 eq), THF, $-70^\circ$	$CH_3COCl$	$(CH_3O)_2P(O)CH(OCOCH_3)C_6H_5$ (70)	36
C <sub>10</sub>	$(CH_3O)_2P(O)OCH_2C_6H_4CH_3-p$	$n-C_4H_9Li$ (1 eq), THF, $-70^\circ$	$CH_3COCl$	$(CH_3O)_2P(O)CH(OCOCH_3)C_6H_4CH_3-p$ (72)	36
C <sub>11</sub>	$(C_2H_5O)_2P(O)OCH_2C_6H_4Cl-p$	$n-C_4H_9Li$ (1 eq), THF, $-70^\circ$	$CH_3COCl$	$(C_2H_5O)_2P(O)CH(OCOCH_3)C_6H_4Cl-p$ (75)	36
	$[(CH_3)_2N]_2P(O)OCH_2C_6H_5$	$n-C_4H_9Li$ (1 eq), THF, $-70^\circ$	$H_2O$	$[(CH_3)_2N]_2P(O)CH(OH)C_6H_5$ (90)	36
		$n-C_4H_9Li$ (2 eq), THF	$CH_3COCl$ $CH_3I$ , then $H_2O$	$[(CH_3)_2N]_2P(O)CH(OCOCH_3)C_6H_5$ (90) $C_6H_5COCH_3$ (-)	36 36
C <sub>12</sub>	$(C_2H_5O)_2P(O)OCH_2C_6H_4OCH_3-o$	$n-C_4H_9Li$ (1 eq), THF, $-70^\circ$	$H_2O$	$(C_2H_5O)_2P(O)CH(OH)C_6H_4OCH_3-o$ (70)	36
	$(C_2H_5O)_2P(O)OCH_2C_6H_4OCH_3-p$	$n-C_4H_9Li$ (1 eq), THF, $-70^\circ$	$H_2O$	$(C_2H_5O)_2P(O)CH(OH)C_6H_4OCH_3-p$ (80)	36
	$[(CH_3)_2N]_2P(O)OCH_2C_6H_4CH_3-p$	$n-C_4H_9Li$ (1 eq), THF, $-70^\circ$	$H_2O$	$[(CH_3)_2N]_2P(O)CH(OH)C_6H_4CH_3-p$ (95)	204
			$CH_3COCl$	$[(CH_3)_2N]_2P(O)CH(OCOCH_3)C_6H_4CH_3-p$ (90)	204
C <sub>14</sub>	$(C_2H_5O)_2P(O)OCH_2$ 	$n-C_4H_9Li$ , THF, $-70^\circ$	$CH_3COCl$	$(C_2H_5O)_2P(O)CH$  (75)	206
				$CH_3CO_2$	

TABLE XVIII. PHOSPHINAMIDES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -70°, 30 min	C <sub>6</sub> H <sub>5</sub> CN	(50)	259
C <sub>10</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -75°, 30 min	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	(75)	39
			CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	+ (20, total)	39

TABLE XIX. PHOSPHINATES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>6</sub>		KOH, C <sub>2</sub> H <sub>5</sub> OH, 80°, 2.5 hr	—	A, B,	A: 64.8, B: 35.2 (—) A: 25, B: 75 (52)	442 442
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, C <sub>2</sub> H <sub>5</sub> OH, 80°, 20 hr	—			
C <sub>8</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.2 eq), THF, -75°	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (2.5 eq)		(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (HO)C (45)	40
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -75°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br		CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (40) " (50)	40, 503 40
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , -75°			" (80-85)	40
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA-THF, 65:35, -75°, 30 min				
			C <sub>6</sub> H <sub>5</sub> CHO		CH(OH)C <sub>6</sub> H <sub>5</sub> (30)	40
			CH <sub>3</sub> COCH <sub>3</sub>		A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (40) A, R = C(OH)(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (55) A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (75) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> (70) A, R = CHO (40) A, R = COC <sub>6</sub> H <sub>5</sub> (35) A, R = CO <sub>2</sub> H (65)	40, 503 40 40 39 39 39 39
			CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>		(40, total)	40
			C <sub>2</sub> H <sub>5</sub> OCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>		(45, total)	40

TABLE XIX. PHOSPHINATES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub> (Contd.)		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA-THF, 65:35, -75°, 30 min	O <sub>2</sub> , -75°, 1 hr, then CH <sub>3</sub> OH, H <sub>2</sub> O	(-)	486
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.2 eq), TMEDA, THF, -70°, 30 min	C <sub>6</sub> H <sub>5</sub> CN, -70°, 1.5 hr, CH <sub>3</sub> OH, H <sub>2</sub> O	(27)	500
186 C <sub>12</sub>	(C <sub>2</sub> H <sub>5</sub> O)(C <sub>3</sub> H <sub>7</sub> - <i>n</i> )P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	NaNH <sub>2</sub> (0.5 eq), ether, -33°	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH=NC <sub>6</sub> H <sub>5</sub>	A, (C <sub>2</sub> H <sub>5</sub> O)(C <sub>3</sub> H <sub>7</sub> - <i>n</i> )P(O)CH(C <sub>6</sub> H <sub>5</sub> )R + B, C <sub>6</sub> H <sub>5</sub> CH=CHR'	476
		NaNH <sub>2</sub> (0.5 eq), ether, 10°		A, (47), R = CH(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> )NHC <sub>6</sub> H <sub>5</sub> , B, (traces), R' = C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	476
		NaNH <sub>2</sub> (0.5 eq), ether, -33°	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub>	A, (0), R = CH(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> )NHC <sub>6</sub> H <sub>5</sub> , B, (16), R' = C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	476
		NaNH <sub>2</sub> (0.5 eq), ether, 10°		A, (72), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> , B, (traces), R' = C <sub>6</sub> H <sub>5</sub>	476
		NaNH <sub>2</sub> (0.5 eq), NH <sub>3</sub> (liq)		A, (45), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> , B, (10), R' = C <sub>6</sub> H <sub>5</sub>	476
		NaNH <sub>2</sub> (0.5 eq), ether, -33°	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	A, (19), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> , B, (10), R' = C <sub>6</sub> H <sub>5</sub>	476
		NaNH <sub>2</sub> (0.5 eq), ether, -33°	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i>	A, (70), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> , B, (-), R' = C <sub>6</sub> H <sub>5</sub>	476
			C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>m</i>	A, (58), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> , B, (traces), R' = C <sub>6</sub> H <sub>5</sub>	476
			C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	A, (60), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>m</i> , B, (traces), R' = C <sub>6</sub> H <sub>5</sub>	476
				A, (81), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> , B, (traces), R' = C <sub>6</sub> H <sub>5</sub>	476
		NaNH <sub>2</sub> (0.5 eq), ether, 10°		A, (20), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> , B, (-), R' = C <sub>6</sub> H <sub>5</sub>	476
C <sub>13</sub>	( <i>i</i> -C <sub>3</sub> H <sub>7</sub> O)(C <sub>3</sub> H <sub>7</sub> - <i>n</i> )P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	NaNH <sub>2</sub> (0.5 eq), ether, -33°	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub>	A, ( <i>i</i> -C <sub>3</sub> H <sub>7</sub> O)( <i>n</i> -C <sub>3</sub> H <sub>7</sub> )P(O)CH(C <sub>6</sub> H <sub>5</sub> )R + B, C <sub>6</sub> H <sub>5</sub> CH=CHR'	476
		NaNH <sub>2</sub> (0.5 eq), ether, 10°		A, (74), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> , B, (traces), R' = C <sub>6</sub> H <sub>5</sub>	476
		NaNH <sub>2</sub> (0.5 eq), ether, 10°	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	A, (47), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> , B, (traces), R' = C <sub>6</sub> H <sub>5</sub>	476
		NaNH <sub>2</sub> (0.5 eq), ether, -33°		A, (68), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> , B, (traces), R' = C <sub>6</sub> H <sub>5</sub>	476
		NaNH <sub>2</sub> (0.5 eq), ether, 10°		A, (29), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> , B, (traces), R' = C <sub>6</sub> H <sub>5</sub>	476
C <sub>15</sub>	(C <sub>6</sub> H <sub>5</sub> )(C <sub>2</sub> H <sub>5</sub> O)P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2.2 eq), C <sub>6</sub> H <sub>6</sub>	O <sub>2</sub> , 1 hr	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (61)	435
C <sub>16</sub>	(C <sub>2</sub> H <sub>5</sub> O)(C <sub>6</sub> H <sub>5</sub> )P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , reflux, 8.5 hr	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> (41)	436
187		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (eq), C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , reflux, 6 hr		(58)	436
C <sub>19</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 15 min	HCl, -70°	C <sub>6</sub> H <sub>5</sub> P(O)(OH)CH <sub>2</sub> C(CH <sub>3</sub> )=C(CH <sub>3</sub> )CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (100)	501
			CH <sub>3</sub> OH, -70°	C <sub>6</sub> H <sub>5</sub> P(O)(OCH <sub>3</sub> )CH <sub>2</sub> C(CH <sub>3</sub> )=C(CH <sub>3</sub> )CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (47)	501
			C <sub>6</sub> H <sub>5</sub> CHO, -70°	(29)	501
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> , -70°	(9.2)	501

TABLE XX. PHOSPHINE OXIDES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>5</sub>		NaOH, 3 <i>N</i> , heat, 24-48 hr	—	A, B, A: 2, B: 3 (—)	545
C <sub>6</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°C, 30 min	CO <sub>2</sub>	(33) +  (18)	545
		NaOH, 3 <i>N</i> , heat, 23 hr	—	A, B, A: 99, B: 1 (—)	545
C <sub>6</sub>		NaOH, 3 <i>N</i> , heat, 27 hr	—	A, B, A: 1, B: 2 (—)	545
		NaOH, 3 <i>N</i> , heat, 27 hr	—	A, B, A: 9, B: 1 (—)	545
C <sub>7</sub>		NaOH, 3 <i>N</i> , heat, 46 hr	—	A, B, A: 9, B: 1 (—)	545
C <sub>10</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -70°, 30 min	C <sub>6</sub> H <sub>5</sub> CN, -70°, 1 hr, then 3 <i>N</i> HCl	(5)	259
C <sub>11</sub>		NaOH, 3 <i>N</i> , heat, 48 hr	—	A, B, A: 5.5, B: 1 (—)	545
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.5 eq), THF, -75°	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (2.5 eq)	(20)	40
C <sub>12</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.2 eq), THF, -75°	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (2.5 eq)	" (35)	40
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -75°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	(15-10)	40, 503
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA-THF, 65:35, -75°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	" (55)	40

TABLE XX. PHOSPHINE OXIDES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.		
C <sub>12</sub> (Contd.)		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	C <sub>6</sub> H <sub>5</sub> CHO	(40)	40		
			C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	R A, R = COC <sub>6</sub> H <sub>5</sub> (-) A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (35) A, R = C(OH)(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (40) A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (47)	259 40 40 40		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -75°, 30 min	O <sub>2</sub> , -75°, 1 hr, then CH <sub>3</sub> OH, H <sub>2</sub> O	(26)	486		
			CO <sub>2</sub>	(30) +  (30)	39		
			(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)Cl	(-)	40		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.2 eq), TMEDA, THF, -70°, 30 min	C <sub>6</sub> H <sub>5</sub> CN, -70°, 1.5 hr, CH <sub>3</sub> OH, H <sub>2</sub> O	R A, R = C <sub>6</sub> H <sub>5</sub> (42) A, R = C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> - <i>p</i> (50)	500 259		
			<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CN				
		C <sub>14</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (CH <sub>3</sub> )P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub> OK	<i>p</i> -(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CN	A, R = C <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> - <i>p</i> (53)	259
					<i>m,m'</i> - <i>p</i> -(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CN	A, R = C <sub>6</sub> H <sub>2</sub> (OCH <sub>3</sub> ) <sub>2</sub> - <i>m,m'</i> - <i>p</i> (45)	259
						A, R =  (36)	259
	A, R =  (29)				259		
	A, R =  (30)				259		
	(10)				259		
C <sub>15</sub>	CH <sub>2</sub> =C=CHP(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	(CH <sub>3</sub> CuC≡CC <sub>6</sub> H <sub>5</sub> )Li, ether, THF	NH <sub>4</sub> Cl, H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (CH <sub>3</sub> )P(O)NHC <sub>6</sub> H <sub>5</sub> (51) C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (73) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (CH <sub>3</sub> )PO <sub>2</sub> H (21) CH <sub>2</sub> =CRCH <sub>2</sub> P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> A, R = CH <sub>3</sub> (45) A: 9, R = CH <sub>3</sub> , A: 1, R = C <sub>6</sub> H <sub>5</sub> (90)	438		
C <sub>15</sub>	CH <sub>2</sub> =C=CHP(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	(CH <sub>3</sub> CuC≡CC <sub>6</sub> H <sub>5</sub> )Li, ether, THF	NH <sub>4</sub> Cl, H <sub>2</sub> O	CH <sub>2</sub> =C(CH <sub>3</sub> )CH[P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ]CH[P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ]C(CH <sub>3</sub> )=CH <sub>2</sub> (42)	165		
		(CH <sub>3</sub> ) <sub>2</sub> CuLi, THF, 0°	—				
		[(CH <sub>3</sub> ) <sub>2</sub> Cu]Li, THF, -10°	NH <sub>4</sub> Cl, H <sub>2</sub> O	CH <sub>2</sub> =CRCH <sub>2</sub> P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> A, R = CH <sub>3</sub> (49) A, R = CH <sub>3</sub> (80)	165 166		
		[(CH <sub>3</sub> ) <sub>2</sub> Cu]Li, THF-ether, 1:1, -20°, 20 min	NH <sub>4</sub> Cl				
		(CH <sub>3</sub> CuC <sub>6</sub> H <sub>5</sub> - <i>n</i> )Li, THF-ether, 1:1, -20°, 20 min	NH <sub>4</sub> Cl	A: 15, R = CH <sub>3</sub> , A: 85, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (80)	166, 482		
		(CH <sub>3</sub> CuC <sub>3</sub> H <sub>7</sub> - <i>i</i> )Li, THF-ether, 1:1, -20°, 20 min	NH <sub>4</sub> Cl	A: 10, R = CH <sub>3</sub> , A: 90, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (82)	166		
		(CH <sub>3</sub> CuC <sub>4</sub> H <sub>9</sub> - <i>t</i> )Li, THF-ether, 1:1, -20°, 20 min	NH <sub>4</sub> Cl	A, R = C <sub>4</sub> H <sub>9</sub> - <i>t</i> (85)	166		



TABLE XX. PHOSPHINE OXIDES (Continued)




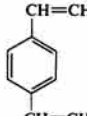


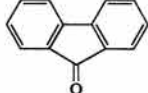
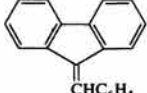
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>15</sub> (Contd.)	CH <sub>2</sub> =C=CHP(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	( <i>i</i> -C <sub>4</sub> H <sub>9</sub> CuC <sub>3</sub> H <sub>7</sub> - <i>i</i> )Li, THF-ether, 1:1, -20°, 20 min	NH <sub>4</sub> Cl	A: 80, R = C <sub>4</sub> H <sub>9</sub> - <i>t</i> , A: 20, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (78)	166	
		( <i>i</i> -C <sub>3</sub> H <sub>7</sub> CuC <sub>4</sub> H <sub>9</sub> - <i>n</i> )Li, THF-ether, 1:1, -20°, 20 min	NH <sub>4</sub> Cl	A: 60, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> , A: 40, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (90)	166	
		(CH <sub>3</sub> CuC≡CC <sub>6</sub> H <sub>5</sub> )Li, THF-ether, 1:1, -20°, 20 min	NH <sub>4</sub> Cl	A, R = CH <sub>3</sub> (75)	166	
		[(CH <sub>3</sub> ) <sub>2</sub> Cu]Li, THF-ether, 1:1, -20°, 20 min	H <sub>2</sub> O	A, CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> + B, (CH <sub>3</sub> ) <sub>2</sub> C=CHP(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> A: 95, B: 5 (100)	166	
C <sub>16</sub>	CH <sub>2</sub> =C=C(CH <sub>3</sub> )P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	[(CH <sub>3</sub> ) <sub>2</sub> Cu]Li, THF, -10°	CH <sub>3</sub> I C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub> NH <sub>4</sub> Cl, H <sub>2</sub> O	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(CH <sub>3</sub> )P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (88) CH <sub>2</sub> =C(CH <sub>3</sub> )CH[P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ](C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (66) CH <sub>2</sub> =C(CH <sub>3</sub> )CH(CH <sub>3</sub> )P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (71)	166 166 165	
		[(CH <sub>3</sub> ) <sub>2</sub> Cu]Li	NH <sub>4</sub> Cl	CH <sub>3</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> <i>cis</i> : 20, <i>trans</i> : 80	166	
	CH <sub>3</sub> CH=C=CHP(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	[( <i>i</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Cu]Li	NH <sub>4</sub> Cl	CH <sub>3</sub> CH=C(C <sub>4</sub> H <sub>9</sub> - <i>t</i> )CH <sub>2</sub> P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> <i>cis</i> : 25, <i>trans</i> : 75 (80)	166	
		CH <sub>3</sub> Li (1 eq), THF, -70°, 30 min. Cul (1 eq), -20°, 5 min	H <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=CHP(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (50)	166	
	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	CH <sub>3</sub> Li (1 eq), -20°	CH <sub>2</sub> =CHCH <sub>2</sub> Br	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(R)PO(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (40)	166	
			CH <sub>3</sub> I C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub>	A, R = CH <sub>3</sub> (45) A, R = CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (45)	166 166	
	CH <sub>3</sub> CH=CHCH <sub>2</sub> P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	<i>cis</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	 , -70° to 25°	 (72)	492
			<i>trans</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	C <sub>6</sub> H <sub>5</sub> SSC <sub>6</sub> H <sub>5</sub>	( <i>E</i> ): 3, ( <i>Z</i> ): 97 ( <i>E</i> ): 97, ( <i>Z</i> ): 3 (-) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)C(CH <sub>3</sub> )=CHCH <sub>2</sub> SC <sub>6</sub> H <sub>5</sub> (-)
	C <sub>18</sub>	C <sub>2</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ( <i>E</i> )	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°		 ( <i>E</i> ): 95, ( <i>Z</i> ): 5 (-)	492
	C <sub>19</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH(CH <sub>3</sub> )C(CH <sub>3</sub> )=CHCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li	C <sub>6</sub> H <sub>5</sub> CHO	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)C(CH <sub>3</sub> )[CH(OH)(C <sub>6</sub> H <sub>5</sub> )]C(CH <sub>3</sub> )=CHCH <sub>3</sub> (-)	393
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> - <i>m,m'</i>		<i>i</i> -C <sub>4</sub> H <sub>9</sub> OK (1.8 eq), C <sub>6</sub> H <sub>6</sub>	O <sub>2</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PO <sub>2</sub> H (88) + <i>m,m'</i> -Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH=CHC <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> - <i>m,m'</i> (78) C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (48)	435	
C <sub>19</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), (CH <sub>3</sub> ) <sub>2</sub> NCHO, room temperature, 20 min	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (52)	436	
			100°, 2 hr Room temperature, 5 hr	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> C≡CC <sub>6</sub> H <sub>5</sub> (37) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHC <sub>6</sub> H <sub>5</sub> (52)	436 436
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), (CH <sub>3</sub> ) <sub>2</sub> NCHO, room temperature, 20 min	C <sub>6</sub> H <sub>4</sub> (CHO) <sub>2</sub> - <i>p</i>	 (51)	436	
			<i>i</i> -C <sub>4</sub> H <sub>9</sub> OK, C <sub>6</sub> H <sub>6</sub> , reflux, 9 hr		 (47)	38
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	Reflux, 14 hr Reflux, 10 hr <i>i</i> -C <sub>4</sub> H <sub>9</sub> OK (1.5 eq), C <sub>6</sub> H <sub>6</sub> , 1 hr	C <sub>6</sub> H <sub>5</sub> CHO C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (70) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHC <sub>6</sub> H <sub>5</sub> (70)	38 38	
				 (43)	38	
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	Reflux, 14 hr Reflux, 10 hr <i>i</i> -C <sub>4</sub> H <sub>9</sub> OK (1.5 eq), C <sub>6</sub> H <sub>6</sub> , 1 hr	C <sub>6</sub> H <sub>5</sub> CH=CHCHO C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> C <sub>2</sub> H <sub>5</sub> COCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (46) C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CHC <sub>6</sub> H <sub>5</sub> (60) C <sub>6</sub> H <sub>5</sub> CH=C(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub> (53)	38 38 38	
			<i>i</i> -C <sub>4</sub> H <sub>9</sub> OK (1.7 eq), C <sub>6</sub> H <sub>6</sub> , room temperature, 2 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub> , reflux, 4 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)NHC <sub>6</sub> H <sub>5</sub> (55) + C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (50)	435
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub> OK (1.7 eq), C <sub>6</sub> H <sub>6</sub> , room temperature, 2 hr	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (33)	434	

TABLE XX. PHOSPHINE OXIDES (Continued)


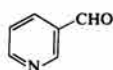

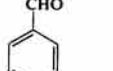

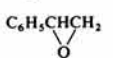
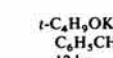
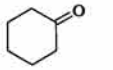


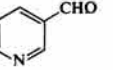


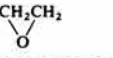

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>19</sub> (Contd.)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), C <sub>6</sub> H <sub>6</sub> , reflux, 1 hr	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OOH (1.2 eq)	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (56) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PO <sub>2</sub> H (80) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH(NO <sub>2</sub> )C <sub>6</sub> H <sub>5</sub> (62)	435 257	
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , 0°, Reflux, 12 hr	C <sub>2</sub> H <sub>5</sub> ONO <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> NO- <i>p</i>	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> N=CHC <sub>6</sub> H <sub>5</sub> (-) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PO <sub>2</sub> H (73) C <sub>6</sub> H <sub>5</sub> CH=C(C <sub>6</sub> H <sub>5</sub> )C(C <sub>6</sub> H <sub>5</sub> )=CHC <sub>6</sub> H <sub>5</sub> (50) CH=CHC <sub>6</sub> H <sub>5</sub>	38 38	
		Reflux, 7 hr	C <sub>6</sub> H <sub>5</sub> COCOC <sub>6</sub> H <sub>5</sub>			38
		Reflux, 12 hr	C <sub>6</sub> H <sub>4</sub> (CHO) <sub>2</sub> - <i>p</i>		 (57)	38
					 (58)	38
					 (47)	38
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1.1 eq), C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , reflux, 12 hr	C <sub>6</sub> H <sub>5</sub> CHCH <sub>2</sub> 	C <sub>6</sub> H <sub>5</sub> -  -C <sub>6</sub> H <sub>5</sub> (37)	228
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1.5 eq), C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , reflux, 6 hr	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (85)	436
			Reflux, 5 hr	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CHC <sub>6</sub> H <sub>5</sub> (76)	436
			Reflux, 4.5 hr		 (55)	436
			Reflux, 3 hr	C <sub>6</sub> H <sub>4</sub> (CHO) <sub>2</sub> - <i>p</i>	 (50)	436
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , reflux, 9 hr		 (55)	436
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , reflux, 9 hr	C <sub>6</sub> H <sub>5</sub> NHN=CHC <sub>6</sub> H <sub>4</sub> CHO- <i>p</i>	 (76) CH=NNHC <sub>6</sub> H <sub>5</sub>	436
			C <sub>6</sub> H <sub>5</sub> Li, ether	C <sub>6</sub> H <sub>5</sub> CHO	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PO <sub>2</sub> H (76) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>5</sub> )R A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> <i>erythro</i> (5), <i>threo</i> (90) (-) A, R = CH <sub>2</sub> CH <sub>2</sub> OH (91)	38, 302
			C <sub>6</sub> H <sub>5</sub> Li, ether	CH <sub>2</sub> CH <sub>2</sub> 	A, R = CH(C <sub>6</sub> H <sub>5</sub> )CH(OH)C <sub>6</sub> H <sub>5</sub> (85)	228
			Reflux, 5 hr C <sub>6</sub> H <sub>5</sub> Li, THF	O <sub>2</sub> , -10°, 15 min, then H <sup>+</sup> CO <sub>2</sub> , then H <sup>+</sup> C <sub>6</sub> H <sub>5</sub> CHCH <sub>2</sub> 	A, R = OH (42) A, R = CO <sub>2</sub> H (65) A, R = CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> OH (60)	435 38 228
			Reflux Reflux, 45 min <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, room temperature, 1 hr	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl, reflux C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br, reflux, 45 min C <sub>6</sub> H <sub>5</sub> COCl, reflux, 1 hr	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (34) A, R = COC <sub>6</sub> H <sub>5</sub> (-)	334 334 254
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li (1.2 eq), THF, TMEDA, room temperature	C <sub>6</sub> H <sub>5</sub> CN	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (72) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)NH <sub>2</sub> (70)	500
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> CH=C=CHP(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> [(CH <sub>3</sub> ) <sub>2</sub> Cu]Li	NH <sub>4</sub> Cl	<i>t</i> -C <sub>4</sub> H <sub>9</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> <i>cis</i> : 30, <i>trans</i> : 70 (18)	166

TABLE XX. PHOSPHINE OXIDES (Continued)

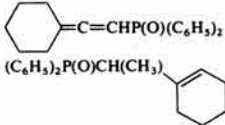

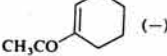
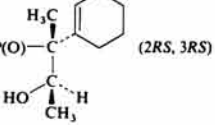
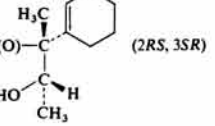
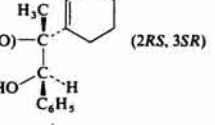
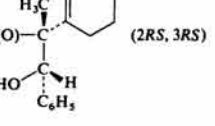
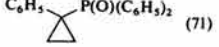
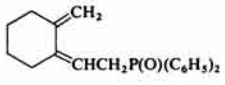
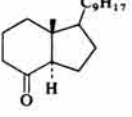
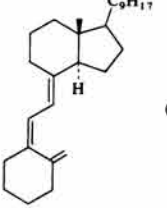
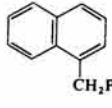
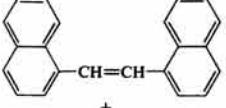

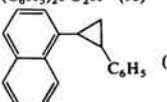
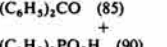
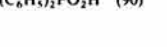
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>20</sub>		[(CH <sub>3</sub> ) <sub>2</sub> Cu]Li, THF, -10°	NH <sub>4</sub> Cl, H <sub>2</sub> O	 (41)	165
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li	O <sub>2</sub>	 (-)	262, 393
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -78°, 30 min	CH <sub>3</sub> CHO	 (2RS, 3RS) +  (2RS, 3SR)	262, 303
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -78°	C <sub>6</sub> H <sub>5</sub> CHO	 (2RS, 3SR) +  (2RS, 3RS)	262, 303 393
C <sub>21</sub>	C <sub>6</sub> H <sub>5</sub> CH=C=CHP(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	[(CH <sub>3</sub> ) <sub>2</sub> Cu]Li	NH <sub>4</sub> Cl	C <sub>6</sub> H <sub>5</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	165, 166
		( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> P added	NH <sub>4</sub> Cl	<i>cis</i> : 37, <i>trans</i> : 63 (75)	
		[( <i>t</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Cu]Li	NH <sub>4</sub> Cl	<i>trans</i> (80)	166
	CH <sub>2</sub> =C=C(C <sub>6</sub> H <sub>5</sub> )P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	[(CH <sub>3</sub> ) <sub>2</sub> Cu]Li, THF, -10°	NH <sub>4</sub> Cl, H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH=C(C <sub>6</sub> H <sub>5</sub> - <i>t</i> )CH <sub>2</sub> P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	166
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH(CH <sub>3</sub> )C(CH <sub>3</sub> )=CHC <sub>4</sub> H <sub>9</sub> - <i>n</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li	C <sub>6</sub> H <sub>5</sub> CHO	<i>cis</i> : 20, <i>trans</i> : 80 (95) CH <sub>2</sub> =C(CH <sub>3</sub> )CH(C <sub>6</sub> H <sub>5</sub> )P(O)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (53)	165
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>5</sub> )C <sub>2</sub> H <sub>5</sub> Cl	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1.25 eq), C <sub>6</sub> H <sub>6</sub> , room temperature, 3 hr	—	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)C(CH <sub>3</sub> )[CH(OH)(C <sub>6</sub> H <sub>5</sub> )]C(CH <sub>3</sub> )=CHC <sub>4</sub> H <sub>9</sub> - <i>n</i> (-)	393	
			C <sub>6</sub> H <sub>5</sub>  (71)	228	
C <sub>22</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°		 (70)	492
C <sub>23</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1.8 eq), C <sub>6</sub> H <sub>6</sub>	O <sub>2</sub>	 (90)	435
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1.1 eq), C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , reflux, 12 hr	C <sub>6</sub> H <sub>5</sub> CHCH <sub>2</sub> 		 (63)
C <sub>25</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1.8 eq), C <sub>6</sub> H <sub>6</sub>	O <sub>2</sub> , 50 min	 (85) +  (90)	435

TABLE XX. PHOSPHINE OXIDES (Continued)

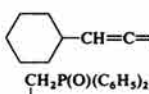
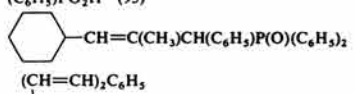
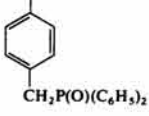
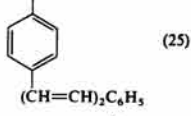
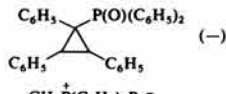
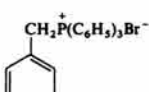
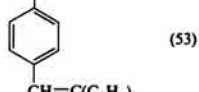

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>25</sub> (Contd.)	$n\text{-C}_6\text{H}_9\text{CH}=\text{C}=\text{C}(\text{C}_6\text{H}_5)\text{P}(\text{O})(\text{C}_6\text{H}_5)_2$	$[(\text{CH}_3)_2\text{Cu}]\text{Li}$ , THF, $-10^\circ$	$\text{NH}_4\text{Cl}, \text{H}_2\text{O}$	$n\text{-C}_6\text{H}_9\text{CH}=\text{C}(\text{CH}_3)\text{CH}(\text{C}_6\text{H}_5)\text{P}(\text{O})(\text{C}_6\text{H}_5)_2$ (16)	165
	$i\text{-C}_4\text{H}_9\text{CH}=\text{C}=\text{C}(\text{C}_6\text{H}_5)\text{P}(\text{O})(\text{C}_6\text{H}_5)_2$	$[(\text{CH}_3)_2\text{Cu}]\text{Li}$	$\text{NH}_4\text{Cl}$	$i\text{-C}_4\text{H}_9\text{CH}=\text{C}(\text{CH}_3)\text{CH}(\text{C}_6\text{H}_5)\text{P}(\text{O})(\text{C}_6\text{H}_5)_2$ <i>trans</i> (16)	166
C <sub>27</sub>	$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{C}_6\text{H}_5)=\text{CHC}_6\text{H}_5$	$i\text{-C}_4\text{H}_9\text{OK}$ (2 eq), $\text{C}_2\text{H}_5\text{OH}$	$\text{O}_2$	$\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{CH}=\text{CHC}(\text{C}_6\text{H}_5)=\text{CHC}_6\text{H}_5$ (16) + $(\text{C}_6\text{H}_5)\text{PO}_2\text{H}$ (93)	435
861 C <sub>32</sub>		$[(\text{CH}_3)_2\text{Cu}]\text{Li}$ , THF, $-10^\circ$	$\text{NH}_4\text{Cl}, \text{H}_2\text{O}$	 (50) $(\text{CH}=\text{CH})_2\text{C}_6\text{H}_5$	165, 166
		$i\text{-C}_4\text{H}_9\text{OK}$ , $\text{C}_6\text{H}_5\text{CH}_3$ , reflux, 9 hr	$\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$	 (25) $(\text{CH}=\text{CH})_2\text{C}_6\text{H}_5$ + $(\text{C}_6\text{H}_5)_2\text{PO}_2\text{H}$ (80)	437
C <sub>33</sub>	$(\text{C}_6\text{H}_5)_2\text{C}=\text{C}=\text{C}(\text{C}_6\text{H}_5)\text{P}(\text{O})(\text{C}_6\text{H}_5)_2$	$[(\text{CH}_3)_2\text{Cu}]\text{Li}$ , THF, $-10^\circ$	$\text{NH}_4\text{Cl}, \text{H}_2\text{O}$	$(\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{CH}_3)\text{CH}(\text{C}_6\text{H}_5)\text{P}(\text{O})(\text{C}_6\text{H}_5)_2$ (69)	165
	$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{Cl}$	$i\text{-C}_4\text{H}_9\text{OK}$ (1.3 eq), $\text{C}_6\text{H}_6$ , 90 min, reflux	—	 (—)	228
C <sub>38</sub>		$i\text{-C}_4\text{H}_9\text{OK}$ (4 eq), $(\text{CH}_3)_2\text{NCHO}$ , 45 min	$\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$ , 24 hr	 (53) + $(\text{C}_6\text{H}_5)_2\text{PO}_2\text{H}$ (65)	437
					

TABLE XXI. PHOSPHINE SULFIDES

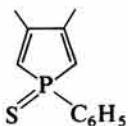
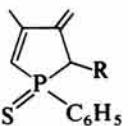
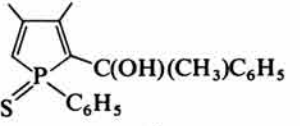
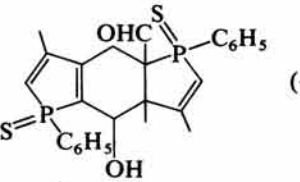
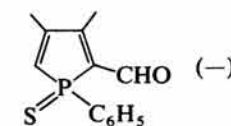
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>12</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 30 min	CH <sub>3</sub> CHO, -70°, 3 hr, then -20°, H <sub>3</sub> O <sup>+</sup>	 A, R = CH(OH)CH <sub>3</sub> (15) A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (8)	502 502
			C <sub>6</sub> H <sub>5</sub> CHO, -70°, 3 hr, then -20°, H <sub>3</sub> O <sup>+</sup>	A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (25)	502
			CH <sub>3</sub> COCH <sub>3</sub> , -70°, 3 hr, then -20°, H <sub>3</sub> O <sup>+</sup>		
			C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> , -70°, 3 hr, then 20°, H <sub>3</sub> O <sup>+</sup>	 (10)	502
			HCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , -70°, 3 hr	 (-)	502
				 (-)	

TABLE XXI. PHOSPHINE SULFIDES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>12</sub> (Contd.)		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -70°, 30 min	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> , -70°, 3 hr, then -20°, H <sub>3</sub> O <sup>+</sup>	 (-)	502
			CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , -70°, 3 hr	(25)	502
			CO <sub>2</sub>	(12)	502
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°		(7)	259
			(10)		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -70°, 30 min	C <sub>6</sub> H <sub>5</sub> CN	(62)	259
				(25)	259
				(20)	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.2 eq), THF, -75°	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (2.5 eq)	(33)	39
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -75°, 30 min	C <sub>6</sub> H <sub>5</sub> CHO	(36)	39

TABLE XXI. PHOSPHINE SULFIDES (Continued)

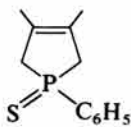
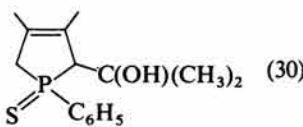
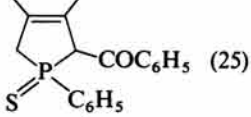
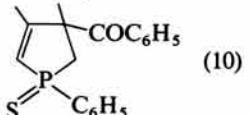
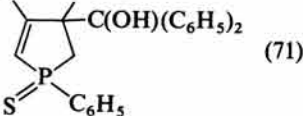
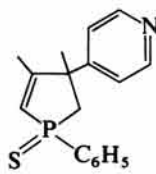
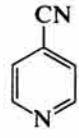
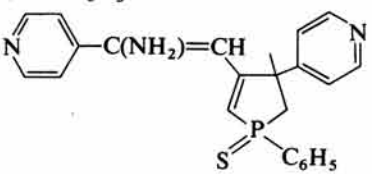
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>12</sub> (Contd.)			CH <sub>3</sub> COCH <sub>3</sub>	 (30)	39
			C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	 (25)	39
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	 (10)	
				 (71)	39
C <sub>17</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1.2 eq), -70°		 (85)	259

TABLE XXII. PHOSPHINOTHIOATES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Ref.
C <sub>19</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	CH <sub>3</sub> I	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH(CH <sub>3</sub> )C <sub>3</sub> H <sub>7-<i>n</i></sub> (57) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SCH <sub>3</sub> (54) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)C(CH <sub>3</sub> )(SCH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (11) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH <sub>3</sub> (14) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SC <sub>4</sub> H <sub>9-<i>n</i></sub> (12)	50



TABLE XXIII. PHOSPHONAMIDES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>7</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	<i>t</i> -C <sub>4</sub> H <sub>9</sub> CHO	A, + B,	42
			C <sub>6</sub> H <sub>5</sub> CHO	A: (30), B: (30), R = CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>t</i>	42
			CH <sub>3</sub> COCH <sub>3</sub>	A: (85), B: (0), R = CH(OH)C <sub>6</sub> H <sub>5</sub>	42
			CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub>	A: (-), B: (0), R = C(OH)(CH <sub>3</sub> ) <sub>2</sub>	42
				A: (-), B: (0), R = C(OH)(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	42
			CH <sub>3</sub> COC <sub>4</sub> H <sub>9</sub> - <i>t</i>	A: (0), B: (-), R = C(OH)(CH <sub>3</sub> )C <sub>4</sub> H <sub>9</sub> - <i>t</i>	42
				A: (0), B: (90), R =	42
	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)CH <sub>2</sub> CH=CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Na, C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , THF, 0°, 2 hr	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> COCH <sub>3</sub>	A: (0), B: (-), R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> A, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)CH=CHCH <sub>2</sub> C(OH)(CH <sub>3</sub> ) <sub>2</sub> + B, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)CH[C(OH)(CH <sub>3</sub> )]CH=CH <sub>2</sub>	42
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>3</sub> COCH <sub>3</sub>	A: (-), B: (0)	42
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>3</sub> COCH <sub>3</sub>	A: (-), B: (0)	42
		CdI <sub>2</sub> , -78°, 30 min, then -20°, 20 min	CH <sub>3</sub> COCH <sub>3</sub>	A: (-), B: (0) (lower yield)	42
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>3</sub> COCH <sub>3</sub>	A: 1, B: 3, (-)	42
		MgBr <sub>2</sub> , -78°, 15 min, -20°, 45 min	CH <sub>3</sub> COCH <sub>3</sub>		42

TABLE XXIV. PHOSPHONATES

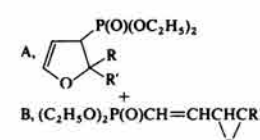
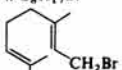
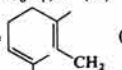
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>5</sub>	(CH <sub>3</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=CHCl	C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> COC <sub>6</sub> H <sub>5</sub>	(CH <sub>3</sub> O) <sub>2</sub> P(O)CH=CHCH <sub>2</sub> CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (25)	244
C <sub>7</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C≡CH	C <sub>2</sub> H <sub>5</sub> SNa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH, reflux, 15 min	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=C(CH <sub>3</sub> )SC <sub>2</sub> H <sub>5</sub> (—)	41
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C(Br)=CHBr	C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH, reflux, 6 hr	H <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=C(OC <sub>2</sub> H <sub>5</sub> )CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> (70)	580
		(CH <sub>3</sub> ) <sub>2</sub> NH, ether, room temperature, 1 hr	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=C[N(CH <sub>3</sub> ) <sub>2</sub> ]CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> (—)	580
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C(Br)=CH <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> MgBr, ether, 5°, 1.5 hr	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=C=CH <sub>2</sub> (45)	580
		NaH, ether, room temperature, 1 hr	HCl, H <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)C≡CCH <sub>3</sub> (90)	580
		C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH, reflux, 6 hr	H <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=CRCH <sub>3</sub> A, R = OC <sub>2</sub> H <sub>5</sub> (75)	580
		<i>i</i> -C <sub>3</sub> H <sub>7</sub> ONa, <i>i</i> -C <sub>3</sub> H <sub>7</sub> OH, reflux, 6 hr	H <sub>2</sub> O	A, R = OC <sub>3</sub> H <sub>7-<i>i</i></sub> (80)	580
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, reflux, 6 hr	H <sub>2</sub> O	A, R = OC <sub>4</sub> H <sub>9-<i>t</i></sub> (82)	580
		(CH <sub>3</sub> ) <sub>2</sub> NH, ether, room temperature, 3 hr	—	A, R = N(CH <sub>3</sub> ) <sub>2</sub> (—)	580
		(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=CHBr	C <sub>2</sub> H <sub>5</sub> ONa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH, reflux, 1 hr C <sub>6</sub> H <sub>5</sub> ONa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH, reflux, 1 hr (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH (3 eq), THF, reflux, 6 hr C <sub>2</sub> H <sub>5</sub> SNa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH, reflux, 1 hr	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=CHR A, R = OC <sub>2</sub> H <sub>5</sub> (66) A, R = OC <sub>6</sub> H <sub>5</sub> (84) A, R = N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (80) A, R = SC <sub>2</sub> H <sub>5</sub> (68)
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=CHCl	C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>5</sub> CHO	 A, (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=CHCH <sub>2</sub> CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> B, (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=CHCH <sub>2</sub> CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> A: 65, B: 35, R = H, R' = C <sub>6</sub> H <sub>5</sub> (63)	244
C <sub>8</sub>		C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i>	A: 35, B: 65, R = CH <sub>3</sub> , R' = C <sub>6</sub> H <sub>5</sub> (51) A: 35, B: 65, R = CH <sub>3</sub> , R' = C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (40) A: 35, B: 65, R = CH <sub>3</sub> , R' = C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> (34)	244 244 244
		Piperidine (2 eq), THF, reflux, 6 hr	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=CHCH <sub>2</sub> N <sub>1</sub> (81)	41
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30 to -80°	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(C <sub>4</sub> H <sub>9-<i>n</i></sub> )CH=CHCl (30)	244
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=CH <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=CHCH <sub>3</sub> (43)	445
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C≡CCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> ONa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=C(OC <sub>2</sub> H <sub>5</sub> )C <sub>2</sub> H <sub>5</sub> (—)	41
		C <sub>2</sub> H <sub>5</sub> SNa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C(OC <sub>2</sub> H <sub>5</sub> )=CHCH <sub>3</sub> (—) (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C(SC <sub>2</sub> H <sub>5</sub> )=CHCH <sub>3</sub> (—)	41
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C(Br)=CHCH <sub>3</sub>	NaH, ether, room temperature, 1 hr	HCl, H <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=C=CHCH <sub>3</sub> (9)	580
		C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH, reflux, 6 hr	H <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C≡CCH <sub>3</sub> (78) (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=C(OC <sub>2</sub> H <sub>5</sub> )C <sub>2</sub> H <sub>5</sub> (77)	580
		(CH <sub>3</sub> ) <sub>2</sub> NH, ether, room temperature, 3 hr	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=C[N(CH <sub>3</sub> ) <sub>2</sub> ]C <sub>2</sub> H <sub>5</sub> (—)	580
		(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C(CH <sub>3</sub> )=CHBr	Piperidine (2 eq), THF, reflux, 6 hr C <sub>2</sub> H <sub>5</sub> ONa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH, reflux, 1 hr C <sub>2</sub> H <sub>5</sub> SNa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH, reflux, 1 hr C <sub>6</sub> H <sub>5</sub> SNa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH, reflux, 1 hr	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=C(CH <sub>3</sub> )CH <sub>2</sub> N <sub>1</sub> (78)
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=C(CH <sub>3</sub> )Cl	C <sub>2</sub> H <sub>5</sub> ONa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH, reflux, 2 hr C <sub>2</sub> H <sub>5</sub> SNa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH, reflux, 2 hr	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C(CH <sub>3</sub> )=CHR A, R = OC <sub>2</sub> H <sub>5</sub> (83) A, R = SC <sub>2</sub> H <sub>5</sub> (62) A, R = SC <sub>6</sub> H <sub>5</sub> (71)	41 41 41
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=C(CH <sub>3</sub> )Cl	C <sub>2</sub> H <sub>5</sub> ONa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH, reflux, 2 hr C <sub>2</sub> H <sub>5</sub> SNa (1.2 eq), C <sub>2</sub> H <sub>5</sub> OH, reflux, 2 hr	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=CH(OC <sub>2</sub> H <sub>5</sub> )C <sub>2</sub> H <sub>5</sub> (60) (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=C(CH <sub>3</sub> )SC <sub>2</sub> H <sub>5</sub> (56)	41 41
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=CHCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -60°, 1 hr	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br, -60°, 30 min, then room temperature <i>n</i> -C <sub>8</sub> H <sub>17</sub> Br	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CHRCH=CHCH <sub>3</sub> A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (83) A, R = C <sub>8</sub> H <sub>17-<i>n</i></sub> (92)	299 299
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=CHCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH	 (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CHCH <sub>2</sub> Br	A, R =  (78)	299
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=CHCH <sub>3</sub> or (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=CHC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH	—	A, R = CH <sub>2</sub> CH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (35) (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=CHCH <sub>3</sub> (7) + (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH=CHC <sub>2</sub> H <sub>5</sub> (25)	299 445

TABLE XXIV. PHOSPHONATES (Continued)


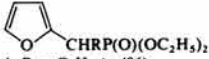
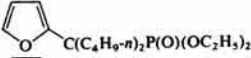
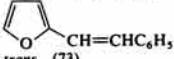
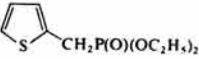



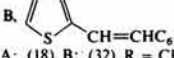

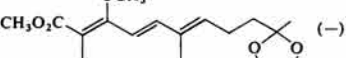
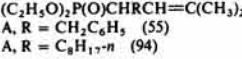
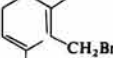
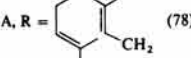
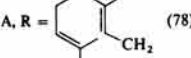
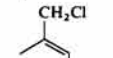
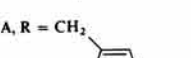


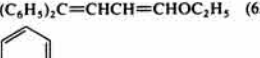



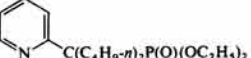

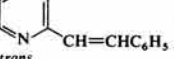
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>9</sub>		NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 30 min	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br, 2 hr	 A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (96)	485	
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 2 hr C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl, 2 hr	A, R = C <sub>6</sub> H <sub>5</sub> - <i>n</i> (97) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (64)	485 485	
		NaNH <sub>2</sub> (2.5 eq), NH <sub>3</sub> (liq)	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br (2.4 eq)	 (94)	232	
			C <sub>6</sub> H <sub>5</sub> CHO	 <i>trans</i> (73)	597	
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 30 min	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br, 2 hr	 A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (91)	485	
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 2 hr	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (95)	485	
		NaNH <sub>2</sub> (0.5 eq), ether, -10° NaNH <sub>2</sub> (0.5 eq), ether, -33°	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub>	A,  +		
			C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> Cl- <i>o</i> C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i>	B,  A: (18), B: (32), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> A: (84), B: (-), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> A: (14), B: (20), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> A: (54), B: (-), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> Cl- <i>o</i> A: (60), B: (12), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> A: (22), B: (27), R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i>	477 477 477 477 477 477	
	(CH <sub>3</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C(OCH <sub>3</sub> )=C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub>	Base (?), THF, +23°		 (-)	398	
			(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -60°, 1 hr	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	 A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (55) A, R = C <sub>6</sub> H <sub>11</sub> - <i>n</i> (94)
			<i>n</i> -C <sub>8</sub> H <sub>17</sub> Br		A, R =  (78)	299
					A, R = CH <sub>2</sub>  (67)	299
(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=CHOC <sub>2</sub> H <sub>5</sub>	NaH, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, heat	THPO	<i>i</i> -C <sub>3</sub> H <sub>7</sub> CHO	<i>i</i> -C <sub>3</sub> H <sub>7</sub> CH=CHCH=CHOC <sub>2</sub> H <sub>5</sub> (57)	150	
		C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHOC <sub>2</sub> H <sub>5</sub> (48)	150	
		<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CHCH=CHOC <sub>2</sub> H <sub>5</sub> (47)	150	
		<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHCH=CHOC <sub>2</sub> H <sub>5</sub> (48)	150	
	NaH, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, heat	C <sub>2</sub> H <sub>5</sub> COCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> (CH <sub>3</sub> )C=CHCH=CHOC <sub>2</sub> H <sub>5</sub> (33)	150		
			 (37)	150		
C <sub>10</sub>		K, C <sub>6</sub> H <sub>6</sub> , 70-80°	C <sub>2</sub> H <sub>5</sub> I	 A, R = C <sub>2</sub> H <sub>5</sub> (50)	499	
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br, 2 hr	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (76) A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (87)	499 485
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 30 min	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 2 hr C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl, 2 hr	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (91) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (92)	485 485	
			NaNH <sub>2</sub> (2.5 eq), NH <sub>3</sub> (liq), 30 min	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br (2.5 eq)	 (91)	485
		NaOH, 50% H <sub>2</sub> O, CH <sub>2</sub> Cl <sub>2</sub> , ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	C <sub>6</sub> H <sub>5</sub> CHO	 <i>trans</i> (71)	534	

TABLE XXIV. PHOSPHONATES (Continued)


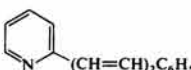
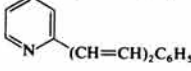
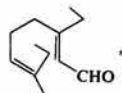
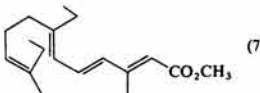
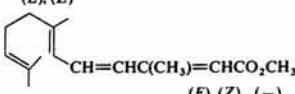

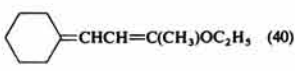
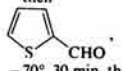
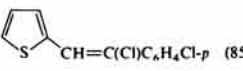


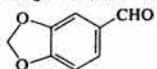
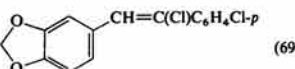
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>10</sub> (Contd.)		NaOH, 50% H <sub>2</sub> O, CH <sub>2</sub> Cl <sub>2</sub> , (n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	C <sub>6</sub> H <sub>5</sub> CH=CHCHO	 (68)	534	
		NaOH, 50% H <sub>2</sub> O, C <sub>6</sub> H <sub>6</sub> , (n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	C <sub>6</sub> H <sub>5</sub> CH=CHCHO	 (75)	157	
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C(CH <sub>3</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (E)	LDA, THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 2:1, 65°		 (78)	143	
	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH <sub>2</sub> C(CH <sub>3</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (Z)	CH <sub>3</sub> ONa, CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> CHO, (CH <sub>3</sub> ) <sub>2</sub> NCHO	C <sub>2</sub> H <sub>5</sub> CH=CHC(CH <sub>3</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (83) (E), (Z)	529	
	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH <sub>2</sub> C(CH <sub>3</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (E):3, (Z):2	30-35°, 45 min	(CH <sub>3</sub> ) <sub>2</sub> NCHO	 (E) (Z) (-)	529	
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> P(O)CH <sub>2</sub> C(CH <sub>3</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (E):3, (Z):2	30-35°, 45 min	C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> CHO, (CH <sub>3</sub> ) <sub>2</sub> NCHO, 40°, 2 hr	C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C(CH <sub>3</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (E): 85, (Z): 15 (-)	528		
(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> ONa, CH <sub>3</sub> OH, 30-35°, 45 min	C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> CHO, (CH <sub>3</sub> ) <sub>2</sub> NCHO, 40°, 2 hr	C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> CH=C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub> (-)	528		
	CH <sub>3</sub> ONa	OHCC(CH <sub>3</sub> )=CHCH=CHCH=C(CH <sub>3</sub> )CHO (0.5 eq)	CH <sub>3</sub> O <sub>2</sub> CC(CH <sub>3</sub> )=CHCH=CHC(CH <sub>3</sub> )=CHCH=CHCH=C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub> (-)	323		
(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=C(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub>	NaH, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, heat	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CHCH=C(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> (40)	150		
			 (40)	150		
		C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHCH=C(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> (47)	150		
C <sub>11</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br-p	n-C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 15 min	CCl <sub>4</sub> , -75°, then 70°, 15 min, then H <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(Cl)C <sub>6</sub> H <sub>4</sub> Br-p (82)	236	
			CCl <sub>4</sub> , -75°, then 70°, 15 min, then CH <sub>3</sub> I, -75°, then room temperature	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)C(Cl)(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> Br-p (83)	236	
		NaOH, 50% H <sub>2</sub> O, C <sub>6</sub> H <sub>6</sub> , (n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	C <sub>6</sub> H <sub>5</sub> CH=CHCHO	C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br-p (81)	157	
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl-o	n-C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 15 min	CCl <sub>4</sub> , -75°, then 70°, 15 min, then room temperature	i-C <sub>3</sub> H <sub>7</sub> CH=C(Cl)C <sub>6</sub> H <sub>4</sub> Cl-o (20)	236	
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl-p	n-C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 15 min	CCl <sub>4</sub> , -75°, then 70°, 15 min, then H <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(Cl)C <sub>6</sub> H <sub>4</sub> Cl-p (85)	236	
		"	CCl <sub>4</sub> , -75°, then 70°, 15 min, then CH <sub>3</sub> I, -75°, then room temperature	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)C(Cl)(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> Cl-p (90)	236	
		"	CCl <sub>4</sub> , -75°, then 70°, 15 min, then		 (85)	236
		n-C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 15 min	CCl <sub>4</sub> , -75°, then 70°, 15 min, then		 (73)	236
		"	CCl <sub>4</sub> , -75°, then 70°, 15 min, then		 (69)	236
		"	-70°, 30 min, then room temperature, 60 min			
		"	-70°, 30 min, then room temperature, 60 min, then i-C <sub>3</sub> H <sub>7</sub> CHO	i-C <sub>3</sub> H <sub>7</sub> CH=C(Cl)C <sub>6</sub> H <sub>4</sub> Cl-p (80)	236	
		"	-70°, 30 min, then room temperature, 60 min, then sec-C <sub>4</sub> H <sub>9</sub> CHO	sec-C <sub>4</sub> H <sub>9</sub> CH=C(Cl)C <sub>6</sub> H <sub>4</sub> Cl-p (87)	236	
	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -p	C <sub>2</sub> H <sub>5</sub> ONa; (CH <sub>3</sub> ) <sub>2</sub> NCHO	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -p cis: (2), trans: (75)	597	
		p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -p cis: (0), trans: (16)	597		
(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	n-C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 15 min	CCl <sub>4</sub> , -75°, then 70°, 15 min, then H <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(Cl)C <sub>6</sub> H <sub>5</sub> (90)	236		
		CCl <sub>4</sub> , -75°, then 70°, 15 min, i-C <sub>3</sub> H <sub>7</sub> CHO, -70°, 30 min, room temperature, 60 min	i-C <sub>3</sub> H <sub>7</sub> CH=C(Cl)C <sub>6</sub> H <sub>5</sub> (69)	236		

TABLE XXIV. PHOSPHONATES (Continued)


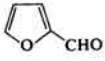
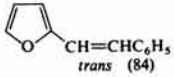
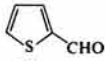
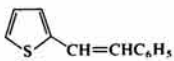
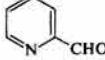
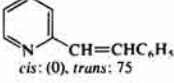

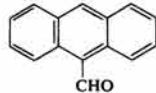
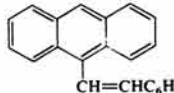
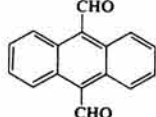
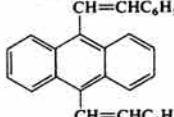
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>11</sub> (Contd.)	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 5 min	S <sub>8</sub> , -20°	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>5</sub> )SH (81)	258c
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.2 eq), THF, TMEDA, room temperature	C <sub>6</sub> H <sub>5</sub> CN, reflux, 24 hr	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (72)	500
		NaH, CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , reflux, 30 min	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> <i>trans</i> (63)	149
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , room temperature, 20 min	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHC <sub>6</sub> H <sub>5</sub> (78)	149
			C <sub>6</sub> H <sub>5</sub> CH=CHCHO	C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (58)	149
			C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (80)	436
		Room temperature, 30 min	C <sub>6</sub> H <sub>5</sub> CH=CHCHO	C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (80)	436
		Room temperature, 5 hr	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHC <sub>6</sub> H <sub>5</sub> (67) CH=CHC <sub>6</sub> H <sub>5</sub>	436
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , room temperature, 20 min	OHCC <sub>6</sub> H <sub>4</sub> CHO- <i>p</i>	 (78)	436
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , reflux, 12 hr	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	CH=CHC <sub>6</sub> H <sub>5</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHC <sub>6</sub> H <sub>5</sub> (70)
		CH <sub>3</sub> ONa, (CH <sub>3</sub> ) <sub>2</sub> NCHO, room temperature, 1-2 hr		 <i>trans</i> (84)	577, 597
				 (77)	577
				 <i>cis</i> : (0), <i>trans</i> : 75	577, 597
		NaBr added <i>m,p</i> -(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO, 90°	C <sub>6</sub> H <sub>5</sub> CHO	<i>cis</i> : (0), <i>trans</i> : (14) C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (OCH <sub>3</sub> ) <sub>2</sub> - <i>m,p</i> <i>cis</i> : (0), <i>trans</i> : (92)	597
			<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> <i>cis</i> : (1), <i>trans</i> : (87)	577, 597
			<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i> <i>cis</i> : (8), <i>trans</i> : (36)	597
			OHCC <sub>6</sub> H <sub>4</sub> CHO- <i>p</i>	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> <i>cis</i> : (0), <i>trans</i> : (100) CH=CHC <sub>6</sub> H <sub>5</sub>	597
			<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	 <i>trans</i> (74) C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> - <i>p</i> <i>trans</i> (80)	597
			C <sub>6</sub> H <sub>5</sub> CH=CHCHO	C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHC <sub>6</sub> H <sub>5</sub> <i>trans</i> (76)	597
				 <i>trans</i> (59) CH=CHC <sub>6</sub> H <sub>5</sub>	597
	 <i>trans</i> (79) CH=CHC <sub>6</sub> H <sub>5</sub>		597		
NaNH <sub>2</sub> (0.5 eq), ether, 10-15°, 1 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> Cl- <i>m</i>		(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>5</sub> )CH(C <sub>6</sub> H <sub>5</sub> )NHR	473	
	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>		A, R = C <sub>6</sub> H <sub>4</sub> Cl- <i>m</i> (88)	473	
	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i>	A, R = C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (81)	473		
	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>m</i>	A, R = C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> (60)	473		
	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub>	A, R = C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>m</i> (87) A, (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>5</sub> )CH(C <sub>6</sub> H <sub>5</sub> )NHR (77) + B, C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> A : (69), B : (20), R = C <sub>6</sub> H <sub>5</sub> A : (58), B : (<1) (-)	473, 476 473, 476		

TABLE XXIV. PHOSPHONATES (Continued)

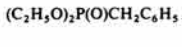

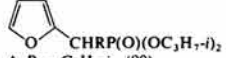
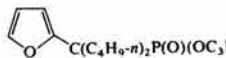

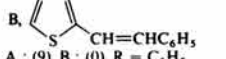


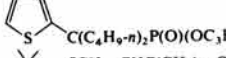
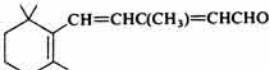
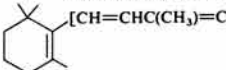
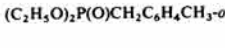
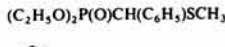

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.		
C <sub>11</sub> (Contd.)		NaNH <sub>2</sub> (0.5 eq), ether, 10°	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	A : (0), B : (16), R = C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	476		
		NaNH <sub>2</sub> (1 eq), C <sub>6</sub> H <sub>6</sub> , reflux, 6 hr	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (0.5 eq)	C <sub>6</sub> H <sub>5</sub> CH=C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (88)	243		
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	C <sub>6</sub> H <sub>5</sub> Br	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (23)	232		
		LiNH <sub>2</sub> , NH <sub>3</sub> (liq)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=NCOC <sub>6</sub> H <sub>5</sub> , ether, -50°, 5 hr, then H <sub>3</sub> O <sup>+</sup>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>5</sub> )C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHCOC <sub>6</sub> H <sub>5</sub> (93)	135		
		LiNH <sub>2</sub> , ether	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=NCOC <sub>6</sub> H <sub>5</sub> , ether, -50°, 5 hr, then H <sub>3</sub> O <sup>+</sup>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>5</sub> )C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHCOC <sub>6</sub> H <sub>5</sub> (76)	135		
		NaOH, 50% H <sub>2</sub> O, C <sub>6</sub> H <sub>6</sub> , (n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	C <sub>6</sub> H <sub>5</sub> CH=CHCHO	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (72)	157		
			NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 30 min	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br, 2 hr	 A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (90) A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (93) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (59) A, R = C <sub>6</sub> H <sub>5</sub> (37) A, R = C <sub>6</sub> H <sub>5</sub> (28)	485 485 485 233 233	
			Na (2 eq), NH <sub>3</sub> (liq), 30 min	C <sub>6</sub> H <sub>5</sub> Br, 2 hr C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl, 2 hr C <sub>6</sub> H <sub>5</sub> Br (2 eq) C <sub>6</sub> H <sub>5</sub> Br			
			NaNH <sub>2</sub> (2.5 eq), NH <sub>3</sub> (liq), 30 min	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br (2.5 eq)	 (93)	485	
			NaNH <sub>2</sub> (0.5 eq), ether, -10°	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub>	A,  + B,  A : (9), B : (0), R = C <sub>6</sub> H <sub>5</sub> A : (15), B : (30), R = C <sub>6</sub> H <sub>5</sub> A : (75), B : (0), R = C <sub>6</sub> H <sub>5</sub> A : (33), B : (-), R = C <sub>6</sub> H <sub>4</sub> Cl- <i>o</i> A : (60), B : (-), R = C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> A : (15), B : (-), R = C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> A : (32), B : (-), R = C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	477 477 477 477 477 477 477	
214		Ether, 0° NH <sub>3</sub> (liq) Ether, 0°	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> Cl- <i>o</i> C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>				
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 30 min	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br, 2 hr	 A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (90) A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (91) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (60)	485 485 485		
		NaNH <sub>2</sub> (2.5 eq), NH <sub>3</sub> (liq), 30 min	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br (2.5 eq)	 (95)	485		
		CH <sub>3</sub> ONa, (CH <sub>3</sub> ) <sub>2</sub> NCHO	 CH=CHC(CH <sub>3</sub> )=CHCHO	 [CH=CHC(CH <sub>3</sub> )=CH] <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (-)	325		
		C <sub>12</sub>		NaNH <sub>2</sub> (0.5 eq), NH <sub>3</sub> (liq), 2 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub> , then NH <sub>4</sub> Cl	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> )R A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> (68) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (47) A, R = CH(C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> )NHC <sub>6</sub> H <sub>5</sub> (-) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> (-) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>m</i> (29) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (-) (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> )CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> <i>erythro</i> (47), <i>threo</i> (2)	475 475 475 475 475 475 475 474
				NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub> , ether, -33°	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> <i>trans</i> (10) (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CHR(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> ) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> (47) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (70)	475 475
				NaNH <sub>2</sub> (0.5 eq), NH <sub>3</sub> (liq)	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i>	A, R = CH(C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> )NHC <sub>6</sub> H <sub>5</sub> (72) A, R = CH(C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> )NHC <sub>6</sub> H <sub>5</sub> (73) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (77) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (76) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> (68) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> (28) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>m</i> (70) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>m</i> (43) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (25) C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (15) C <sub>6</sub> H <sub>5</sub> CH=C(C <sub>6</sub> H <sub>5</sub> )SCH <sub>3</sub> ( <i>E</i> ): 11, ( <i>Z</i> ): 89 (80)	475 475 475 475 475 475 475 475 475 258c
				NaNH <sub>2</sub> (0.5 eq), NH <sub>3</sub> (liq), 2 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i>		
				NaNH <sub>2</sub> (0.5 eq), ether, -33°, 2.5 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i>		
				-33°, 3.5 hr	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH=NC <sub>6</sub> H <sub>5</sub>		
10°, 75 min	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH=NC <sub>6</sub> H <sub>5</sub>						
-33°, 2 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>						
10°, 1.5 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>						
-33°, 2.5 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i>						
0°, 24 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i>						
-33°, 2.5 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i>						
10°, 105 min	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>m</i>						
-33°, 4.5 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>						
10°, 5 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>						
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 5 min	C <sub>6</sub> H <sub>5</sub> CHO, reflux						
215		NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 30 min	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br, 2 hr	 A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (90)	485		

TABLE XXIV. PHOSPHONATES (Continued)


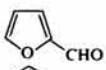
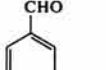
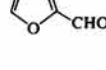
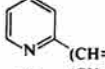
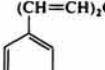
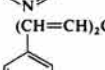
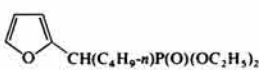
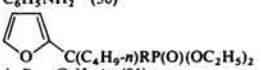
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>12</sub> (Contd.)		NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 30 min	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, 2 hr C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl, 2 hr	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (94) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (88)	485 485	
		NaNH <sub>2</sub> (2.5 eq), NH <sub>3</sub> (liq), 30 min CH <sub>3</sub> ONa (2 eq) <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , room temperature, 3 hr Reflux, 6 hr Reflux, 9 hr	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br (2.5 eq) (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CHCOCH <sub>3</sub> (2 eq) C <sub>6</sub> H <sub>5</sub> CH=CHCHO C <sub>6</sub> H <sub>5</sub> CH=CHCHO C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> CHO	(89) (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CHC(CH <sub>3</sub> )=CHCH=C(CH <sub>3</sub> )CH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (-) C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (5)	485 323 436	
216 C <sub>13</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> ONa, (CH <sub>3</sub> ) <sub>2</sub> NCHO, room temperature, 1.2 hr	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (20) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHCH=CHCH=C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (61) C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> <i>trans</i> (-)	436 436 597	
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, C <sub>2</sub> H <sub>5</sub> OH	     	 (38)  (59)  (59)  (52) C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i> (59)  (84)	157 157 157 157 157	
		NaOH, 50% H <sub>2</sub> O, C <sub>6</sub> H <sub>6</sub> , ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	  	 (55)  (12)	157 157	
			C <sub>6</sub> H <sub>5</sub> CHO <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO C <sub>6</sub> H <sub>5</sub> CH=CHCHO C <sub>6</sub> H <sub>5</sub> Br	C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (70) C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i> (55) C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (80) ( <i>n</i> -C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> P(O)CHRC <sub>6</sub> H <sub>5</sub> A, R = C <sub>6</sub> H <sub>5</sub> (21) A, R = Cl(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHCOC <sub>6</sub> H <sub>5</sub> (65)	157 157 157 232 135	
		( <i>n</i> -C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=NCOC <sub>6</sub> H <sub>5</sub> , ether, -50°, 5 hr, then H <sub>3</sub> O <sup>+</sup>	A, R = C <sub>6</sub> H <sub>5</sub> (21) A, R = Cl(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHCOC <sub>6</sub> H <sub>5</sub> (65)	232 135
		( <i>i</i> -C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	LiNH <sub>2</sub> , NH <sub>3</sub> (liq) 5 hr, then H <sub>3</sub> O <sup>+</sup> NaNH <sub>2</sub> (0.5 eq), NH <sub>3</sub> (liq) NaNH <sub>2</sub> (0.5 eq), ether, 10-15°, 1 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub>	( <i>i</i> -C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> P(O)CHRC <sub>6</sub> H <sub>5</sub> A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> (85) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> (64)	477 473
			LiNH <sub>2</sub> , NH <sub>3</sub> (liq)	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> Cl- <i>m</i> C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>m</i> C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> Cl- <i>m</i> (59) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (73) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> (52) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>m</i> (52) A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (33)	473 473 473 473
			LiNH <sub>2</sub> , NH <sub>3</sub> (liq)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=NCOC <sub>6</sub> H <sub>5</sub> , ether, -50°, 5 hr, then H <sub>3</sub> O <sup>+</sup>	A, R = Cl(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHCOC <sub>6</sub> H <sub>5</sub> (55)	135
			LiNH <sub>2</sub> , NH <sub>3</sub> (liq), Fe(NO <sub>3</sub> ) <sub>3</sub> (cat) KNH <sub>2</sub> , NH <sub>3</sub> (liq), Fe(NO <sub>3</sub> ) <sub>3</sub> (cat) NaNH <sub>2</sub> , NH <sub>3</sub> (liq), Fe(NO <sub>3</sub> ) <sub>3</sub> (cat), 30 min	C <sub>6</sub> H <sub>5</sub> Br	A, R = C <sub>6</sub> H <sub>5</sub> (6) A, R = C <sub>6</sub> H <sub>5</sub> (17)	232 232
			NaNH <sub>2</sub> (1 eq), NH <sub>3</sub> (liq)	C <sub>6</sub> H <sub>5</sub> Br (30 min)	( <i>i</i> -C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (21) + ( <i>i</i> -C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (62) + C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> (36)	232
C <sub>14</sub>			<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br	 A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (91) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (89)	485 485	
		(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> - <i>p</i>	C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH, reflux C <sub>2</sub> H <sub>5</sub> ONa, (CH <sub>3</sub> ) <sub>2</sub> NCHO	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl C <sub>6</sub> H <sub>5</sub> CHO <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> - <i>p</i> <i>trans</i> (78.5) <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> - <i>p</i> <i>cis</i> : (1.9), <i>trans</i> : (63.5)	597 597

TABLE XXIV. PHOSPHONATES (Continued)

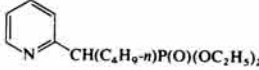
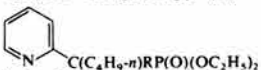

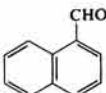
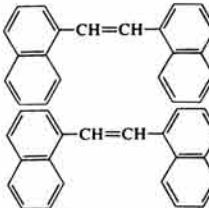
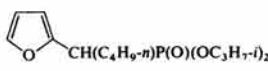
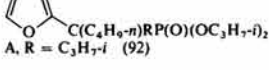
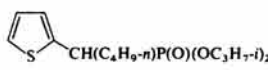
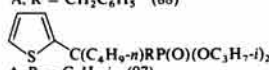
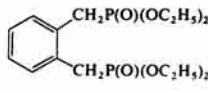
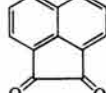
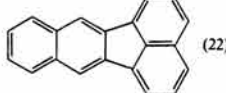

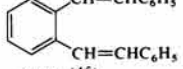
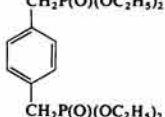
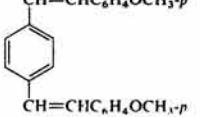
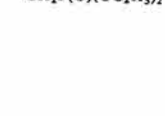
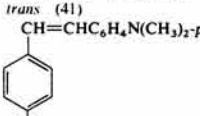

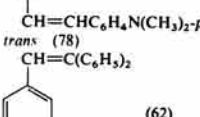
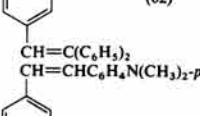
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>14</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> - <i>p</i>	C <sub>2</sub> H <sub>5</sub> ONa, (CH <sub>3</sub> ) <sub>2</sub> NCHO	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO C <sub>6</sub> H <sub>5</sub> CH=CHCHO	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> - <i>p</i> <i>cis</i> : (0), <i>trans</i> : (64.8) C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> - <i>p</i> <i>cis</i> : (0), <i>trans</i> : (85.1)	597 597
	( <i>i</i> -C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	NaNH <sub>2</sub> (0.5 eq), (liq) NaNH <sub>2</sub> (0.5 eq), ether, -33°, 2 hr 10°, 2 hr -33°, 4 hr 10°, 4.5 hr	C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	( <i>i</i> -C <sub>3</sub> H <sub>7</sub> O) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> )CH(C <sub>6</sub> H <sub>5</sub> )NHR A, R = C <sub>6</sub> H <sub>5</sub> (71) A, R = C <sub>6</sub> H <sub>5</sub> (76) A, R = C <sub>6</sub> H <sub>5</sub> (69) A, R = C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (76) C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (18)	475 475 475 475 475
218 C <sub>15</sub>		NaNH <sub>2</sub> (1 eq), NH <sub>3</sub> (liq)	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	 A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (92) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (91)	485 485
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2.2 eq), C <sub>6</sub> H <sub>6</sub> CH <sub>3</sub> ONa, (CH <sub>3</sub> ) <sub>2</sub> NCHO	O <sub>2</sub> , 3 hr 	 (50) <i>cis</i> : (6), <i>trans</i> : (67)	435 597 232
C <sub>15</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ( <i>sec</i> -C <sub>4</sub> H <sub>9</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	NaNH <sub>2</sub> , NH <sub>3</sub> (liq) LiNH <sub>2</sub> , ether NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	C <sub>6</sub> H <sub>5</sub> Br (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=NCOC <sub>6</sub> H <sub>5</sub> , ether, -50°, 5 hr, then H <sub>3</sub> O <sup>+</sup> C <sub>6</sub> H <sub>5</sub> Br	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> O) <sub>2</sub> P(O)CH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (18) ( <i>sec</i> -C <sub>4</sub> H <sub>9</sub> O) <sub>2</sub> P(O)CHRC <sub>6</sub> H <sub>5</sub> A, R = C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHCOC <sub>6</sub> H <sub>5</sub> (58) A, R = C <sub>6</sub> H <sub>5</sub> (18)	135 232
		NaNH <sub>2</sub> (1 eq), NH <sub>3</sub> (liq)	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br	 A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (92)	485
C <sub>16</sub>		NaNH <sub>2</sub> (1 eq), NH <sub>3</sub> (liq)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl <i>i</i> -C <sub>3</sub> H <sub>7</sub> Br	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (88)  A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (97) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (91)	485
		CH <sub>3</sub> ONa, (CH <sub>3</sub> ) <sub>2</sub> NCHO, 0°, 1 hr		 (22)	602
219 C <sub>16</sub>		Room temperature, 1-2 hr	C <sub>6</sub> H <sub>5</sub> CHO	 CH=CHC <sub>6</sub> H <sub>5</sub> <i>trans</i> (45) CH=CHC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i>	597
		CH <sub>3</sub> ONa, (CH <sub>3</sub> ) <sub>2</sub> NCHO	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	 CH=CHC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> <i>trans</i> (41) CH=CHC <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> - <i>p</i>	597
		CH <sub>3</sub> ONa, (CH <sub>3</sub> ) <sub>2</sub> NCHO	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	 CH=CHC <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> - <i>p</i> <i>trans</i> (78) CH=C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	597
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , room temperature, 5 hr	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	 CH=C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH=CHC <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> - <i>p</i> (62)	436
	Room temperature, 20 min	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	 CH=CHC <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> - <i>p</i> (67)	436	



TABLE XXIV. PHOSPHONATES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>16</sub> (Contd.)		Room temperature, 20 min	<i>p</i> -C <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>4</sub> CHO	 (83)	436
		Reflux, 7 hr		 (62)	436
		Reflux, 8 hr	C <sub>6</sub> H <sub>5</sub> CHO	 (69)	436
		Reflux, 7 hr	C <sub>6</sub> H <sub>5</sub> CH=CHCHO	 (84)	436
		Reflux, 7 hr		 (64)	436
		Reflux, 7 hr		 (68)	436
		Reflux, 8 hr	<i>p</i> -C <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>4</sub> CHO	 (92)	436
		Reflux, 8 hr		 (65)	436
		Reflux, 9 hr		 (70)	436
				NaH, CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , reflux, 30 min	C <sub>6</sub> H <sub>5</sub> CHO
		C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH, 35°, 3 hr	C <sub>6</sub> H <sub>5</sub> CH=CHCHO	C <sub>6</sub> H <sub>5</sub> (CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> [(CH=CH) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ]- <i>p</i> (32)	149
				 (50)	569
		NaNH <sub>2</sub> (1 eq), NH <sub>3</sub> (liq)	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br	 A. R = C <sub>2</sub> H <sub>5</sub> - <i>i</i> (89) A. R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (85)	485 485
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	 A. R = C <sub>2</sub> H <sub>5</sub> - <i>i</i> (89) A. R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (85)	485 485

TABLE XXIV. PHOSPHONATES (Continued)

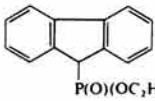
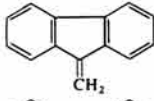
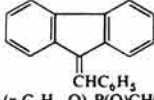

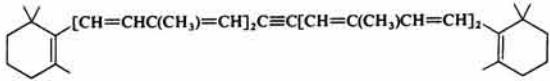
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>17</sub>	$(C_6H_5O)_2P(O)CH_2CH=CHCO_2CH_3$  $P(O)(OC_6H_5)_2$	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> , reflux, 10 hr	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHCO <sub>2</sub> H (52)	38
		NaH, CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , 25°, 30°	CH <sub>2</sub> O	 (77)	149
			C <sub>6</sub> H <sub>5</sub> CHO	 (80)	149
		$(n-C_3H_7O)_2P(O)CH_2C_6H_5$ $(sec-C_3H_7O)_2P(O)CH_2C_6H_5$	NaNH <sub>2</sub> , NH <sub>3</sub> (liq) NaNH <sub>2</sub> , NH <sub>3</sub> (liq) LiNH <sub>2</sub> , NH <sub>3</sub> (liq)	C <sub>6</sub> H <sub>5</sub> Br C <sub>6</sub> H <sub>5</sub> Br $(C_6H_5)_2C=NCOC_6H_5$ , ether, -50°, 5 hr, then H <sub>2</sub> O*	$(n-C_3H_7O)_2P(O)CH(C_6H_5)_2$ (20) $(sec-C_3H_7O)_2P(O)CH(C_6H_5)R$ A, R = C <sub>6</sub> H <sub>5</sub> (20) A, R = C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHCOC <sub>6</sub> H <sub>5</sub> (59)
C <sub>18</sub>	$(C_2H_5O)_2P(O)CH_2C(CH_3)=CHC\equiv C-$ $CH=C(CH_3)CH_2P(O)(OC_2H_5)_2$	NaOCH <sub>3</sub> (2 eq)	 $CH=CHC(CH_3)=CHCHO$ (2 eq)	 (--)	323

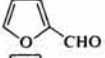
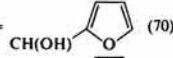
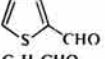
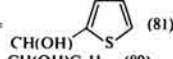
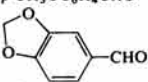
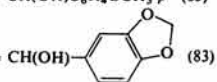


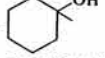
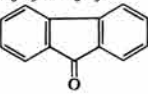
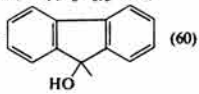
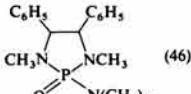
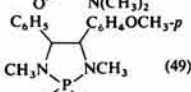
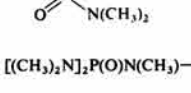
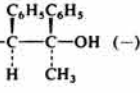
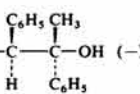
TABLE XXV. PHOSPHINODITHIOATES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>15</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(S)SCH <sub>2</sub> CH=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	—	CH <sub>2</sub> =CHCH <sub>2</sub> SC <sub>4</sub> H <sub>9</sub> - <i>n</i> (63)	415
		C <sub>6</sub> H <sub>5</sub> Li, room temperature	—	C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> CH=CH <sub>2</sub> (72)	415
C <sub>19</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(S)SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	CH <sub>3</sub> I	<i>n</i> -C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-)	50
		C <sub>6</sub> H <sub>5</sub> Li, -78°, room temperature	—	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P(S)CH <sub>3</sub> (-)	415
		C <sub>6</sub> H <sub>5</sub> Li, room temperature	—	C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (79) C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (60)	415 415

TABLE XXVI. PHOSPHORAMIDES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>3</sub> )CH <sub>2</sub> C≡CH (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>3</sub> )CH=C=CH <sub>2</sub> [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CH <sub>2</sub> CH=CH <sub>2</sub>	NaH, THF, reflux, 1.5 hr	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>3</sub> )CH=C=CH <sub>2</sub> (100)	373
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>3</sub> )C(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )=C=CH <sub>2</sub> (80)	373
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -50°, 1.5 hr	H <sub>2</sub> O	A, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CH(R)CH=CH <sub>2</sub> + B, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CH=CHCH <sub>2</sub> R	265
			CH <sub>3</sub> SSCH <sub>3</sub>	A: 40, B: 60, R = H (-)	26
			C <sub>2</sub> H <sub>5</sub> SSC <sub>2</sub> H <sub>5</sub>	A: 25, B: 75, R = SCH <sub>3</sub> (-)	26
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> SSC <sub>4</sub> H <sub>9</sub> - <i>n</i>	A: 1, B: 3, R = SC <sub>2</sub> H <sub>5</sub> (-)	26
			C <sub>6</sub> H <sub>5</sub> SSC <sub>6</sub> H <sub>5</sub>	A: 0, B: 1, R = SC <sub>4</sub> H <sub>9</sub> - <i>n</i> (-)	26
			<i>n</i> -C <sub>8</sub> H <sub>17</sub> Br	A: 0, B: 1, R = SC <sub>6</sub> H <sub>5</sub> (-)	265
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	A: 0, B: 1, R = C <sub>6</sub> H <sub>11</sub> - <i>n</i> (-)	265
			ClCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl- <i>o</i>	A: 0, B: 1, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-)	265
	ClCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	A: 0, B: 1, R = CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl- <i>o</i> (-)	265		
		A: 0, B: 1, R = CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (-)	265		
C <sub>9</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>3</sub> )CH <sub>2</sub> C≡CH (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>3</sub> )C(CH <sub>3</sub> )=C=CH <sub>2</sub> [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub>	NaH, THF, reflux, 1.5 hr	—	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>3</sub> )CH=C=CH <sub>2</sub> (100)	373
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>3</sub> )C(CH <sub>3</sub> )=CHCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (50)	373
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -50°, >1.5 hr	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	A, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CHRC(CH <sub>3</sub> )=CH <sub>2</sub> + B, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CH=C(CH <sub>3</sub> )CH <sub>2</sub> R	265
			CH <sub>3</sub> SSCH <sub>3</sub>	A: 0, B: 1, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-)	26
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> SSC <sub>4</sub> H <sub>9</sub> - <i>n</i>	A: 25, B: 75, R = SCH <sub>3</sub> (-)	26
			C <sub>6</sub> H <sub>5</sub> SSC <sub>6</sub> H <sub>5</sub>	A: 0, B: 1, R = SC <sub>4</sub> H <sub>9</sub> - <i>n</i> (-)	26
			C <sub>6</sub> H <sub>5</sub> SSC <sub>6</sub> H <sub>5</sub>	A: 0, B: 1, R = SC <sub>6</sub> H <sub>5</sub> (-)	26
			(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> Br	A, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CHRC(CH <sub>3</sub> )=CHCH <sub>3</sub> + B, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CH=CHCH(CH <sub>3</sub> )R	265
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	A: 0, B: 1, R = CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> (-)	265
			CH <sub>3</sub> SSCH <sub>3</sub>	A: 0, B: 1, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	26
C <sub>12</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>3</sub> )CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), THF, -70°	H <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>3</sub> )CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-) + CH <sub>3</sub> N=CHC <sub>6</sub> H <sub>5</sub> (-) + CH <sub>3</sub> NHCH(C <sub>6</sub> H <sub>5</sub> )C <sub>6</sub> H <sub>9</sub> - <i>n</i> (-)	28
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, -70°	H <sub>2</sub> O	CH <sub>3</sub> N=CHC <sub>6</sub> H <sub>5</sub> + CH <sub>3</sub> NHCH(C <sub>6</sub> H <sub>5</sub> )C <sub>6</sub> H <sub>9</sub> - <i>n</i> (-) CH <sub>3</sub> NHCH(C <sub>6</sub> H <sub>5</sub> )C <sub>6</sub> H <sub>9</sub> - <i>n</i> (-)	28
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, -70°, inverse addition	H <sub>2</sub> O		28
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -75°, 1.5 hr	CH <sub>2</sub> CHCH <sub>3</sub> 	(C <sub>2</sub> H <sub>5</sub> O)[(CH <sub>3</sub> ) <sub>2</sub> N]P(O)N(CH <sub>3</sub> )CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH(OH)CH <sub>3</sub> (85)	185
			C <sub>6</sub> H <sub>5</sub> CH=NCH <sub>3</sub> , 20 hr, -0°		185
			CH <sub>3</sub> CHO, -78°, then 30 min, room temperature		185
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> CHO	A, R = H, R' = CH <sub>3</sub> (78)	27, 185
			C <sub>6</sub> H <sub>5</sub> CHO	A, R = H, R' = C <sub>6</sub> H <sub>5</sub> - <i>t</i> (65)	27, 185
			<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	A, R = H, R' = C <sub>6</sub> H <sub>5</sub> (68)	27, 185
			<i>o</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	A, R = H, R' = C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (70)	27, 185
	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	A, R = H, R' = C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>o</i> (38)	27, 185		
		A, R = H, R' = C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> (39)	27, 185		
		A, R = R' = (CH <sub>2</sub> ) <sub>4</sub> (41)	185		
		A, R = R' = (CH <sub>2</sub> ) <sub>5</sub> (41)	27		
	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	A, R = R' = C <sub>6</sub> H <sub>5</sub> (80)	27, 185		
	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	A, R = C <sub>6</sub> H <sub>5</sub> , R' = C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (69)	185		
	C <sub>6</sub> H <sub>5</sub> N=CHC <sub>6</sub> H <sub>5</sub> , 2 hr, -30°, then 0°, 3 hr	(C <sub>2</sub> H <sub>5</sub> O)[(CH <sub>3</sub> ) <sub>2</sub> N]P(O)N(CH <sub>3</sub> )CH(C <sub>6</sub> H <sub>5</sub> )CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> (75)	185		
[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 1.5 hr	CH <sub>3</sub> I	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CHRC <sub>6</sub> H <sub>5</sub>	185	
		ClCH <sub>2</sub> OCH <sub>3</sub>	A, R = CH <sub>3</sub> (100)	185	
		<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	A, R = CH <sub>2</sub> OCH <sub>3</sub> (100)	185	
		CH <sub>2</sub> =CHCH <sub>2</sub> Br	A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (80)	185	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (80)	185	
		CH <sub>2</sub> CHCH <sub>3</sub>	A, R = C <sub>6</sub> H <sub>9</sub> - <i>n</i> (80)	185	
			A, R = CH <sub>2</sub> CH(OH)CH <sub>3</sub> (91)	185	
		CH <sub>3</sub> CHO	A, R = CH(OH)CH <sub>3</sub> (76)	185	

TABLE XXVI. PHOSPHORAMIDES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>12</sub> (Contd.)	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 1.5 hr		A, R =  (70)	185
				A, R =  (81)	185
			C <sub>6</sub> H <sub>5</sub> CHO	A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (89)	185
			<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	A, R = CH(OH)C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (87)	185
			<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	A, R = CH(OH)C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> (83)	185
				A, R = CH(OH)-  (83)	185
				No reaction	185
				A, R =  (55)	185
			C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub> (49)	185
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (86)	185
				A, R =  (60)	185
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> ) (82)	185
			C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub> , -20°, 3 hr	A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHC <sub>6</sub> H <sub>5</sub> (80)	185
			<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=NC <sub>6</sub> H <sub>5</sub> , -20°, 3 hr	A, R = CH(C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> )NHC <sub>6</sub> H <sub>5</sub> (92)	185
			C <sub>6</sub> H <sub>5</sub> CH=NCH <sub>3</sub> , -78°, 20 hr	A, R = CH(C <sub>6</sub> H <sub>5</sub> )NHCH <sub>3</sub> (40)	185
-	 (46)	185			
-50°, 20 hr	 (49)	185			
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=NCH <sub>3</sub> , -50°, 20 hr		185			
C <sub>14</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> C≡CH [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> , H <sub>2</sub> O	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )-  (-)	286
				+ [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )-  (-)	
C <sub>14</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> C≡CH [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub>	NaH, THF, reflux, 1.5 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -50°, 1.5 hr	-	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)N(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )CH=C=CH <sub>2</sub> (100)	373
			CH <sub>3</sub> I or (CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub>	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> P(O)N(CH <sub>3</sub> )CH=CHC <sub>6</sub> H <sub>5</sub> (A)	265
			CH <sub>2</sub> =CHCH <sub>2</sub> Br	A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (-)	265
			<i>i</i> -C <sub>3</sub> H <sub>7</sub> Cl	A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (-)	265
			CH <sub>3</sub> SSCH <sub>3</sub>	A, R = SCH <sub>3</sub> (-)	26

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub>		LDA, THF	CH <sub>3</sub> I	A,	
			(CH <sub>3</sub> ) <sub>3</sub> SiCl	B,	144
				A: 70, B: 30, R = CH <sub>3</sub> (-)	144
				A: 60, B: 40, R = Si(CH <sub>3</sub> ) <sub>3</sub> (-)	61, 538
C <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> SeCH <sub>2</sub> C≡CH	C <sub>2</sub> H <sub>5</sub> ONa (0.1 eq), C <sub>2</sub> H <sub>5</sub> OH, 48°, 70 min		C <sub>6</sub> H <sub>5</sub> SeCH=C=CH <sub>2</sub> (59)	61
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> , 83°, 1 hr		C <sub>6</sub> H <sub>5</sub> SeC≡CCH <sub>3</sub> (45)	460
	C <sub>6</sub> H <sub>5</sub> SeCH <sub>2</sub> CH=CH <sub>2</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> , room temperature, 5 hr		C <sub>6</sub> H <sub>5</sub> SeCH=CHCH <sub>3</sub> (91)	
		LDA, THF, -78°, 10 min	C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>3</sub> Br	A, C <sub>6</sub> H <sub>5</sub> SeCHRCH=CH <sub>2</sub>	
				+ B, C <sub>6</sub> H <sub>5</sub> SeCH=CHCH <sub>2</sub> R	144
				A: 80, B: 20, R = (CH <sub>2</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>5</sub> (-)	144
				A: 82, B: 18, R = Si(CH <sub>3</sub> ) <sub>3</sub> (-)	144
			(CH <sub>3</sub> ) <sub>3</sub> SiCl, -78°, 15 min	A: 41, B: 59, R = Si(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-)	144
			(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> SiCl	A: 15, B: 85, R = C(OH)(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> ) (-)	144
			C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> SeC(CH <sub>3</sub> )=C=CH <sub>2</sub> (72)	61, 538
C <sub>10</sub>	C <sub>6</sub> H <sub>5</sub> SeCH(CH <sub>3</sub> )C≡CH	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (0.1 eq), <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, 85°, 1 hr			
	C <sub>6</sub> H <sub>5</sub> SeCH <sub>2</sub> CH=CClCH <sub>3</sub> <i>cis, trans</i>	LDA, THF, -78°, < 5 min	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br, -78°, < 15 min	A, C <sub>6</sub> H <sub>5</sub> SeCHRCH=CClCH <sub>3</sub>	
				+ B, C <sub>6</sub> H <sub>5</sub> SeCH=CHCCl(CH <sub>3</sub> )R (unstable)	144
				A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-)	144
		LDA, THF, -78°, 5 min	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-)	144
			(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> SiCl	A, R = Si(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-)	144
			CH <sub>2</sub> CHCH <sub>3</sub>	A, R = CH <sub>2</sub> CH(OH)CH <sub>3</sub> (-)	144
C <sub>11</sub>	C <sub>6</sub> H <sub>5</sub> SeCH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	LDA, THF, 0°, 20 min	(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> SiCl, -78°, 15 min	A, C <sub>6</sub> H <sub>5</sub> SeCH[SiC <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> ]CH=C(CH <sub>3</sub> ) <sub>2</sub>	
				+ B, C <sub>6</sub> H <sub>5</sub> SeCH=CHC(CH <sub>3</sub> ) <sub>2</sub> [SiC <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> ]	144
				A: 90, B: 10 (-)	
C <sub>13</sub>	C <sub>6</sub> H <sub>5</sub> SeCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	LDA, THF	CH <sub>3</sub> Br	C <sub>6</sub> H <sub>5</sub> SeCHRC <sub>6</sub> H <sub>5</sub>	58
				A, R = CH <sub>3</sub> (-)	58
			C <sub>2</sub> H <sub>5</sub> Br	A, R = C <sub>2</sub> H <sub>5</sub> (-)	58
		LDA, THF, -30°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-)	59
			<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Br, -78°	A, R = C <sub>4</sub> H <sub>9</sub> - <i>sec</i> (not isolated)	59
			CH <sub>2</sub> CHCH <sub>3</sub> ,	A, R = CH <sub>2</sub> CHOHCH <sub>3</sub>	59
				(not isolated)	
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> Br, -78°	A, R = CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (not isolated)	59
			C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>3</sub> Br, -78°	A, R = (CH <sub>2</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>5</sub> (not isolated)	59
C <sub>15</sub>	C <sub>6</sub> H <sub>5</sub> SeCH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub>	LDA, THF, -78°, < 5 min	CH <sub>3</sub> COCH <sub>3</sub> , -78°	A, C <sub>6</sub> H <sub>5</sub> SeCH[COH(CH <sub>3</sub> ) <sub>2</sub> ]CH=CHC <sub>6</sub> H <sub>5</sub>	144
				+ B, C <sub>6</sub> H <sub>5</sub> SeCH=CHCH[COH(CH <sub>3</sub> ) <sub>2</sub> ]C <sub>6</sub> H <sub>5</sub>	
				A: 50, B: 50 (-)	
				CH(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )SeC <sub>6</sub> H <sub>5</sub> (-)	
C <sub>20</sub>		LDA, THF	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br		58

TABLE XXVIII. SELENOXIDES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>13</sub>	C <sub>6</sub> H <sub>5</sub> Se(O)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	LDA, THF-ether, 1:1, -78°	<i>n</i> -C <sub>5</sub> H <sub>11</sub> I, -78°	C <sub>6</sub> H <sub>5</sub> Se(O)CH(C <sub>6</sub> H <sub>5</sub> )R A, R = C <sub>5</sub> H <sub>11</sub> - <i>n</i> (not isolated)	59
			(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Br, -78°	A, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (not isolated)	59
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br, -78°	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (not isolated)	59

TABLE XXIX. SILANES



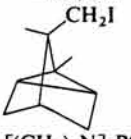
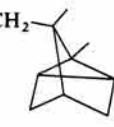
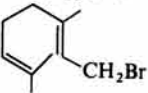
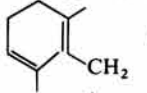
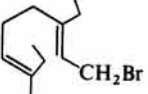
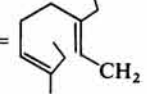
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>6</sub>	(CH <sub>3</sub> ) <sub>3</sub> SiC≡CCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, ether, -15°, 4 hr		RCH <sub>2</sub> C≡CSi(CH <sub>3</sub> ) <sub>3</sub> A, R =  (77)	611	
			[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -20°, 6 hr			A, R =  (-)
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, ether, -5°, 15 min	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -25°, 15 hr	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> I, 0°, 12 hr	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (50)	379
			<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, 0°, 12 hr	A, R = C <sub>6</sub> H <sub>13</sub> - <i>n</i> (55)	379	
				A, R =  (50)	379	
	A, R =  (-)	356				



TABLE XXIX. SILANES (Continued)

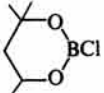
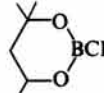
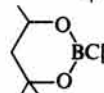
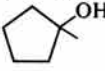
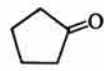
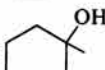
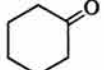
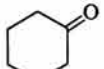
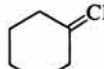
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>6</sub> (Contd.)	(CH <sub>3</sub> ) <sub>3</sub> SiC≡CCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, ether, 0°		 (45) +  (5)	412	
232	(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> CH=CH <sub>2</sub>	Mg (1 eq), (CH <sub>3</sub> ) <sub>3</sub> SiCl (3 eq), TiCl <sub>4</sub> or FeCl <sub>3</sub> (cat), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO	—	(CH <sub>3</sub> ) <sub>3</sub> SiCH=CHCH <sub>2</sub> R A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (58)	396	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, ether, room temperature	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCl	A, R = Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (—)	108	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	A, (CH <sub>3</sub> ) <sub>3</sub> SiCH(R)CH=CH <sub>2</sub> + B, (CH <sub>3</sub> ) <sub>3</sub> SiCH=CHCH <sub>2</sub> R A: 0, B: 100, R = C(OH)(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (—) A: 0, B: 100, R = C(OH)(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (—)	281b 281b	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -78°, 2 hr, ZnCl <sub>2</sub> , -78°, 45 min	—	A: 0, B: 100, R = C(OH)(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (—)	281b	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -78°, 2 hr, CdI <sub>2</sub> , -78°, 45 min	—	A: 92, B: 8, R = C(OH)(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (—)	281b	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -78°, 2 hr, MgBr <sub>2</sub> , -78°, 45 min	—	A: 86, B: 14, R = C(OH)(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (—)	281b	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 2 hr, MgBr <sub>2</sub> , -78°, 45 min	—	A: 95, B: 5, R = C(OH)(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (—)	281b	
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, THF, -78°, 2 hr, MgBr <sub>2</sub> , -78°, 45 min	—	A: 0, B: 100, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (—)	281b	
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, THF, -78°, 2 hr, MgBr <sub>2</sub> , -78°, 45 min	C <sub>6</sub> H <sub>5</sub> CHO	A: 60, B: 40, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (—)	281b	
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, THF, -78°, 2 hr, MgBr <sub>2</sub> , -78°, 45 min	—	(CH <sub>3</sub> ) <sub>3</sub> SiCH=CHCH <sub>2</sub> R A, R = <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH(OH) (—)	284c	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, then -40°	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	A, R =  (77)	284c	
		233	C <sub>7</sub> (CH <sub>3</sub> ) <sub>3</sub> SiCH(CH <sub>3</sub> )CH=CH <sub>2</sub>	Mg (1 eq), (CH <sub>3</sub> ) <sub>3</sub> SiCl (3 eq), TiCl <sub>4</sub> or FeCl <sub>3</sub> (cat), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO	—	(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> CH=C(CH <sub>3</sub> )Si(CH <sub>3</sub> ) <sub>3</sub> (30)
	A, R =  (73)				284c	
	—				(CH <sub>3</sub> ) <sub>3</sub> SiCHDC <sub>6</sub> H <sub>5</sub> (85) C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (50) <i>cis</i> : 1, <i>trans</i> : 2	367 367
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO	D <sub>2</sub> O				(CH <sub>3</sub> ) <sub>3</sub> SiCHDC <sub>6</sub> H <sub>5</sub> (85)	107
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA	C <sub>6</sub> H <sub>5</sub> CHO CH <sub>3</sub> COCH <sub>3</sub>				C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (72) C <sub>6</sub> H <sub>5</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (50)	532 532
C <sub>10</sub>	(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> Li, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 0°		 (52)	532	
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH=C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (77)	532	

TABLE XXIX. SILANES (Continued)

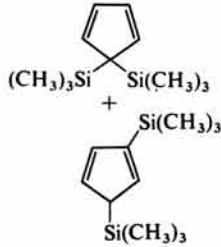
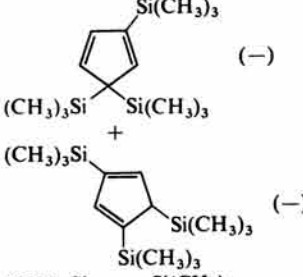
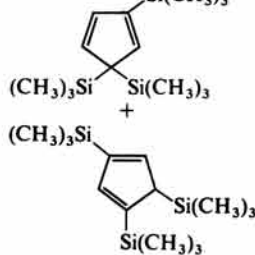
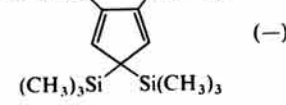
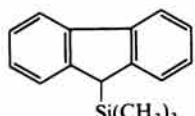
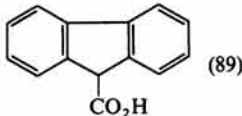
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>10</sub> (Contd.)	(CH <sub>3</sub> ) <sub>3</sub> SiCH(Br)C <sub>6</sub> H <sub>5</sub>	Mg, ether	CH <sub>2</sub> =CHCH <sub>2</sub> Br, reflux, 4.5 hr	(CH <sub>3</sub> ) <sub>3</sub> SiCH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH=CH <sub>2</sub> (74)	425
			(CH <sub>3</sub> CO) <sub>2</sub> O, -60°, 3.5 hr, then warmed to -10°, NH <sub>4</sub> Cl	C <sub>6</sub> H <sub>5</sub> CH(COCH <sub>3</sub> )Si(CH <sub>3</sub> ) <sub>3</sub> (19)	425
			(CH <sub>3</sub> ) <sub>3</sub> SiCHBrC <sub>6</sub> H <sub>5</sub>	(CH <sub>3</sub> ) <sub>3</sub> SiCH(C <sub>6</sub> H <sub>5</sub> )CH(C <sub>6</sub> H <sub>5</sub> )Si(CH <sub>3</sub> ) <sub>3</sub> (35)	425
C <sub>11</sub> 234		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li	(CH <sub>3</sub> ) <sub>3</sub> SiCl		425
C <sub>14</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li	(CH <sub>3</sub> ) <sub>3</sub> SiCl		452
C <sub>16</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, reflux, 16 hr	CO <sub>2</sub> , then H <sub>3</sub> O <sup>+</sup>	 (89)	412
C <sub>21</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>3</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiLi (1 eq), THF, room temperature, 5 hr	H <sub>3</sub> O <sup>+</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH (51) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>3</sub> (18) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (30) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (19) [(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (32)	413
			(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCl	+ (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH (25) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (18) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (9) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>3</sub> (10) (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (16)	413
		(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiLi, THF, ether, 5 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCl	+ (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>3</sub> (29) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH (55) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (15) + [(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (23) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (5)	413

TABLE XXIX. SILANES (Continued)

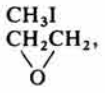
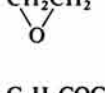
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>21</sub> (Contd.)	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li, THF, room temperature, 5 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH (70) + (C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Si (10) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (-) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>3</sub> (14)	413
			(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCl	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (23) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (13) + (C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Si (12) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>3</sub> (33)	413
236	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH <sub>2</sub> CH=CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Li (1 eq), THF, room temperature, 22 hr	H <sub>3</sub> O <sup>+</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH (29) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=CHCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (40)	413
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, ether, room temperature, 5 hr	HCl, <i>N</i>	A, (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCHRCH=CH <sub>2</sub> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=CHCH <sub>2</sub> R A: 30-40, B: 60-70, R = H (80) A: 0, B: 1, R = CH <sub>3</sub> (80) A: 40, B: 60, R = CH <sub>2</sub> CH <sub>2</sub> OH (70)	108, 255 108, 255 108, 255
			CH <sub>3</sub> I CH <sub>2</sub> CH <sub>2</sub> ,  room temperature, 5° C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> (CH <sub>3</sub> ) <sub>3</sub> SiCl C <sub>6</sub> H <sub>5</sub> CON(CH <sub>3</sub> ) <sub>2</sub>	A: 90, B: 10, R = CH <sub>2</sub> CH <sub>2</sub> OH (70) A: 0, B: 1, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (90) A: 20, B: 80, R = CO <sub>2</sub> H (60) A: 0, B: 1, R = Si(CH <sub>3</sub> ) <sub>3</sub> (80) (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH <sub>2</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub> (50-60)	255 108, 255 108, 255 108, 255 255
	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=CHCH <sub>2</sub> Br	Mg, ether, room temperature	CH <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub> H <sub>2</sub> O CH <sub>3</sub> I CH <sub>2</sub> CH <sub>2</sub> , 	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH <sub>2</sub> CH=CHCOCH <sub>3</sub> (60) (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH <sub>2</sub> CH=CH <sub>2</sub> (80) No reaction A, (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCHRCH=CH <sub>2</sub> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=CHCH <sub>2</sub> R A: 90, B: 10, R = CH <sub>2</sub> CH <sub>2</sub> OH (70) A: 0, B: 1, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (65)	255 255 255 255
			C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> (CH <sub>3</sub> ) <sub>3</sub> SiCl	A: 85, B: 15, R = CO <sub>2</sub> H (60) A: 0, B: 1, R = Si(CH <sub>3</sub> ) <sub>3</sub> (50)	255 255
C <sub>22</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CC <sub>2</sub> H <sub>5</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiLi (1.2 eq), THF, room temperature, 40.5 hr	H <sub>3</sub> O <sup>+</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Si (5) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH (43) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=C(C <sub>2</sub> H <sub>5</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (2) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (2)	413
237	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH <sub>2</sub> CH=CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Li (1.5 eq), THF, room temperature, 19 hr	CH <sub>3</sub> I	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Si (42) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CC <sub>3</sub> H <sub>7-i</sub> (3)	413
		C <sub>6</sub> H <sub>5</sub> Li (1.1 eq), THF, room temperature, 20 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH (81) + (C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Si (48) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CC <sub>2</sub> H <sub>5</sub> (1) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (-) + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=C=C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (15)	413
C <sub>24</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH <sub>2</sub> CH=CHSi(CH <sub>3</sub> ) <sub>3</sub> or (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=CHCH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, ether, room temperature	(CH <sub>3</sub> ) <sub>3</sub> SiCl, 4 hr	A, (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=CHCH[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> + B, [(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si][(CH <sub>3</sub> ) <sub>3</sub> Si]CHCH=CHSi(CH <sub>3</sub> ) <sub>3</sub> A: 88, B: 12 (70-75)	108
C <sub>25</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, reflux, 2 hr	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (80)	37

TABLE XXIX. SILANES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>25</sub> (Contd.)	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, reflux, 2 hr	CO <sub>2</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiOH (52)	37
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, room temperature, 18 hr	CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CO <sub>2</sub> H (43) C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (79)	356
C <sub>31</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, room temperature, 3-4 hr	(CH <sub>3</sub> ) <sub>3</sub> SiCl	C <sub>6</sub> H <sub>5</sub> CH[Si(CH <sub>3</sub> ) <sub>3</sub> ]Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (76)	356
			CO <sub>2</sub> , then H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH(C <sub>6</sub> H <sub>5</sub> )CO <sub>2</sub> H (60)	356
C <sub>31</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, room temperature, 3-4 hr	D <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CDSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (88)	356
			CH <sub>3</sub> I	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (81)	356
C <sub>39</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, room temperature, 40 min	CO <sub>2</sub> , then H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiO <sub>2</sub> CCH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (-)	356
			(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiOH	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCO <sub>2</sub> H (-)	
C <sub>39</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (1 eq), THF, room temperature, 3 hr	(CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (58)	609
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (25)	609
C <sub>39</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (1 eq), THF, room temperature, 3 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCl, 5 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Si (12)	413
			CH <sub>3</sub> I, 1 hr	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (42)	
C <sub>39</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (2 eq), THF, room temperature, 1 hr	CH <sub>3</sub> I, 1 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (28)	413
			(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Si (9)	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC(CH <sub>3</sub> )=C=C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (3)	
C <sub>39</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (2 eq), THF, room temperature, 1 hr	CH <sub>3</sub> I, 1 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (-)	413
			(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (-)		
C <sub>39</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (1 eq), THF, room temperature, 1 hr	CH <sub>3</sub> I, 1 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=C=C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (-)	413
			(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (51)		
C <sub>39</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (1 eq), THF, room temperature, 1 hr	CH <sub>3</sub> I, 1 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=C=C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (-)	413
			(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (51)		
C <sub>39</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (1 eq), THF, room temperature, 3.5 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCl, 3.5 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (58)	413
			(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (3)		
C <sub>40</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=C=C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (2 eq), THF, room temperature, 3 hr	CH <sub>3</sub> I	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH (89)	
			[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (51)		
C <sub>40</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> + (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCH=C=C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (2 eq), THF, room temperature, 3 hr	CH <sub>3</sub> I	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=C[Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> (-)	
			(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC(CH <sub>3</sub> )=C=C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (36)		
C <sub>57</sub>	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (2 eq), THF, room temperature, 3.5 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCl, room temperature, 3.5 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (-)	413
			(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (31)		
C <sub>57</sub>	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (2 eq), THF, room temperature, 3.5 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH (53)	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (-)	
			[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=C[Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> (3)		
C <sub>57</sub>	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (3 eq), THF, room temperature, 3.25 hr	CH <sub>3</sub> I, 1 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CC(CH <sub>3</sub> ) <sub>2</sub> Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (-)	
			[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=C(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (67)		
C <sub>57</sub>	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (2 eq), THF, room temperature, 5 hr	D <sub>2</sub> O	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CDSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (88)	413
			H <sub>3</sub> O <sup>+</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiH (70)	413
C <sub>57</sub>	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (1.3 eq), THF, room temperature, 1.5 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiCl, room temperature, 27 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SiC≡CCH(CH <sub>3</sub> )Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (89)	413
			(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Si (12)		
C <sub>57</sub>	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (1.3 eq), THF, room temperature, 1.5 hr	CH <sub>3</sub> I, 1 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (89)	413
			[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=C[Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> (14)		
C <sub>57</sub>	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Li (1.3 eq), THF, room temperature, 1.5 hr	CH <sub>3</sub> I, 1 hr	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=CHSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> (89)	413
			[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Si] <sub>2</sub> C=C=C[Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> (17)		

TABLE XXX. SULFIMINES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Ref.
C <sub>20</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S(C <sub>6</sub> H <sub>5</sub> )=NSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	NaOH (cat), dioxane-D <sub>2</sub> O, 10:1	—	C <sub>6</sub> H <sub>5</sub> CD <sub>2</sub> S(C <sub>6</sub> H <sub>5</sub> )=NSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (—)	52

TABLE XXXI. SULFONAMIDES

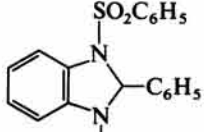
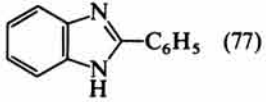
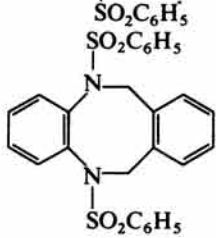
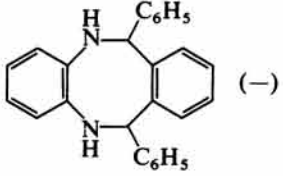
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 0°, then room temperature, 45 min	D <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CR <sub>2</sub> SO <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> A, R = D (81)	55
			CH <sub>3</sub> I (2.2 eq)	A, R = CH <sub>3</sub> (75)	55
			BrCH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> Br	A, R <sub>2</sub> = (CH <sub>2</sub> ) <sub>4</sub> (86)	55
C <sub>19</sub>	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> N(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> Li (1 eq), THF, room temperature, overnight	C <sub>2</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>5</sub> N=CHC <sub>6</sub> H <sub>5</sub> (20) + C <sub>6</sub> H <sub>5</sub> NHCH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (25) + C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> N(C <sub>6</sub> H <sub>5</sub> )NCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (—) C <sub>6</sub> H <sub>5</sub> NHCH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (95)	29
		C <sub>6</sub> H <sub>5</sub> Li (2.3 eq), THF, then C <sub>6</sub> H <sub>5</sub> Li (2.3 eq), room temperature, 5 hr	C <sub>2</sub> H <sub>5</sub> OH		29
C <sub>25</sub>		C <sub>6</sub> H <sub>5</sub> Li (4 eq), THF, room temperature, 5 hr	—	 (77)	29
C <sub>26</sub>		C <sub>6</sub> H <sub>5</sub> Li (20 eq), THF, room temperature, 3 days	—	 (—)	29

TABLE XXXII. SULFONES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>4</sub>		CH <sub>3</sub> OH, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> OH <sup>-</sup> 10 <sup>0</sup> , 3.5 hr	CH <sub>2</sub> =CHCN (4 eq)	(NCCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> (20)	156
C <sub>5</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.1 eq), C <sub>6</sub> H <sub>6</sub> , <i>n</i> -C <sub>6</sub> H <sub>14</sub> , room temperature, 15 min	D <sub>2</sub> O, D <sub>2</sub> SO <sub>4</sub>	(1.16 D) (-)	237
242			CCl <sub>3</sub> CCl <sub>3</sub>	(32) +  (5) +  (32) +  (12)	237
		5% NaOH, H <sub>2</sub> O, 24 hr	-	(67)	402
		(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	-	(45)	402
C <sub>6</sub>		NaCH <sub>2</sub> S(O)CH <sub>3</sub> , CH <sub>3</sub> S(O)CH <sub>3</sub>	-	(-)	71
		NaCH <sub>2</sub> S(O)CH <sub>3</sub> , CH <sub>3</sub> S(O)CH <sub>3</sub>	-	(-)	71
	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SO <sub>2</sub> CH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCOCH <sub>3</sub>	(-)	253
			C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub>	(-)	253
			CH <sub>3</sub> CH=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	(-)	253
			(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	(-)	253
			C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	(-)	253
243	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SO <sub>2</sub> CH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (0.2 eq), THF	C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )CH(SO <sub>2</sub> CH <sub>3</sub> )CH=C(CH <sub>3</sub> ) <sub>2</sub> (-)	253
C <sub>7</sub>		2 N NaOH	H <sub>3</sub> O <sup>+</sup>	(-)	409
C <sub>8</sub>		KOH, C <sub>2</sub> H <sub>5</sub> OH, H <sub>2</sub> O, UV	-	(-)	338
	C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub> CH(CH <sub>3</sub> )CH=CHSO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	KOH, C <sub>2</sub> H <sub>5</sub> OH, H <sub>2</sub> O, UV	-	C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (-)	547
C <sub>9</sub>		CD <sub>3</sub> COCD <sub>3</sub> , D <sub>2</sub> O, 2 hr	-	A, R = D (-)	349
		CH <sub>3</sub> OD, 6 hr	-	A, R = D (-)	349
		CD <sub>3</sub> S(O)CD <sub>3</sub> , D <sub>2</sub> O, 8 hr	-	A, R = D (-)	349
	CH <sub>2</sub> =CHCH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, 89 <sup>0</sup> , or pyridine, 115 <sup>0</sup> , or <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, 25 <sup>0</sup>	-	CH <sub>2</sub> =CHCH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (28) + CH <sub>3</sub> CH=CHSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> <i>cis</i> (3); <i>trans</i> (69)	560

TABLE XXXII. SULFONES (Continued)




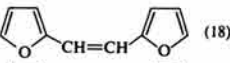
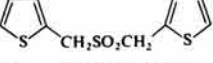
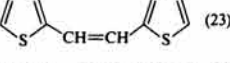
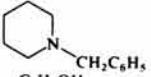



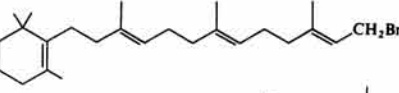
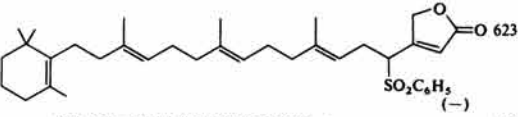

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>10</sub>	 CH <sub>2</sub> =C=CHSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> S(O)CH <sub>3</sub> , 90°, 1 hr	—	 (60-90)	420
		(CH <sub>3</sub> CuCH <sub>3</sub> )Li, ether, THF, 25°, 10 min	NH <sub>4</sub> Cl	CH <sub>2</sub> =CRCH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	482
		(CH <sub>3</sub> CuCH <sub>3</sub> )MgX, ether, THF	NH <sub>4</sub> Cl	A, R = CH <sub>3</sub> (-) A, R = CH <sub>3</sub> (50)	482
		( <i>i</i> -C <sub>3</sub> H <sub>7</sub> CuC <sub>3</sub> H <sub>7</sub> - <i>i</i> )MgX, ether, THF	NH <sub>4</sub> Cl	A, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> (60)	482
		(CH <sub>3</sub> CuR)Li, THF-ether, 1:1, -20°, 20 min	NH <sub>4</sub> Cl	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	166
		R = C≡CC <sub>6</sub> H <sub>5</sub>		CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (85)	166
		R = CN		CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (70)	166
		R = I		CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (70)	166
		(CH <sub>3</sub> CuCH <sub>3</sub> )Li, THF-ether, 1:1, -20°, 20 min	CH <sub>2</sub> =CHCH <sub>2</sub> Br	CH <sub>2</sub> =C(CH <sub>3</sub> )CHRSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (78)	166
		CH <sub>2</sub> =C=CHSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i>	(CH <sub>3</sub> Cu≡CC <sub>6</sub> H <sub>5</sub> )Li, ether, THF	C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> , NH <sub>4</sub> Cl	A, R = CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-) CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> (85)
		(CH <sub>3</sub> CuCN)Li, ether, THF	NH <sub>4</sub> Cl	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> (70)	482
		(CH <sub>3</sub> CuCH <sub>3</sub> )Li, ether, THF	C <sub>6</sub> H <sub>5</sub> CH=CHCOCH <sub>3</sub>	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> )CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> COCH <sub>3</sub> (-)	482
		KOH, CCl <sub>4</sub> , room temperature	—	 (18)	358
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.2 eq), CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> , 0°	CuCl <sub>2</sub> , room temperature	 (23)	358
	CH <sub>2</sub> =CHCH <sub>2</sub> SO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	( <i>n</i> -C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, 120°, 6 hr	—	CH <sub>3</sub> CH=CHSO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (50)	339
		( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> N, C <sub>2</sub> H <sub>5</sub> OH, reflux, 8 hr	—	CH <sub>3</sub> CH=CHSO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (45)	339
			—	CH <sub>3</sub> CH=CHSO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (45)	339
	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> OH, reflux 16 hr	—	CH <sub>3</sub> CH=CHSO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (45)	339
		(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, 89°, or pyridine, 115°, or <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, 25°	—	A, CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> + B, (CH <sub>3</sub> ) <sub>2</sub> C=CHSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> A: 70, B: 30 (-)	560
	CH <sub>2</sub> =CHCH(CH <sub>3</sub> )SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> [(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> ] <sub>2</sub> SO <sub>2</sub>	KOH, CCl <sub>4</sub> , room temperature	—	CH <sub>3</sub> CH=C(CH <sub>3</sub> )SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (100) (CH <sub>3</sub> ) <sub>2</sub> C=CHCH=CHCH=C(CH <sub>3</sub> ) <sub>2</sub> (78)	560 358
C <sub>11</sub>		NaCH <sub>2</sub> S(O)CH <sub>3</sub> , CH <sub>3</sub> S(O)CH <sub>3</sub>	—	 Na <sup>+</sup> (-)	455
		NaCH <sub>2</sub> S(O)CH <sub>3</sub> , CH <sub>3</sub> S(O)CH <sub>3</sub>	—	 Na <sup>+</sup> (-)	455
		NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, 25°			623
	CH <sub>3</sub> CH=C=CHSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	(CH <sub>3</sub> CuCH <sub>3</sub> )Li, THF	NH <sub>4</sub> Cl	CH <sub>3</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> <i>cis</i> : 20, <i>trans</i> : 80 (70)	166
	CH <sub>3</sub> =CHCH(CH <sub>3</sub> )SO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	 , pyridine	—	CH <sub>3</sub> CH=C(CH <sub>3</sub> )SO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (76)	340
CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	140°, 6 hr <i>sec</i> -C <sub>3</sub> H <sub>7</sub> OH, ( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> N, 130°, 16 hr	—	(CH <sub>3</sub> ) <sub>2</sub> C=CHSO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (20)	340	
(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> )SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> Li, THF, -55°	CH <sub>3</sub> I	CH <sub>2</sub> =C(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (63)	624	
CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	CH <sub>3</sub> Li (1 eq), THF, -20°, 30 min	CH <sub>2</sub> =CHCH <sub>2</sub> Br	CH <sub>2</sub> =C(CH <sub>3</sub> )CHRSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (88)	166	
	CuI (1 eq), -20°, 5 min	—	—	166	



TABLE XXXII. SULFONES (Continued)

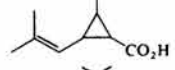

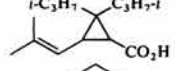
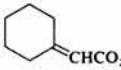


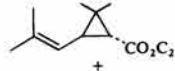
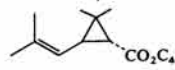
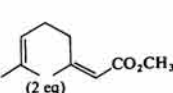
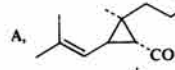
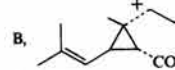
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.		
C <sub>11</sub> (Contd.)	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> ( <i>E</i> ) C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub> Li (1 eq), -20° <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 15 min	C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub> , CH <sub>3</sub> I	A, R = CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (80) A, R = CH <sub>3</sub> (80)	166 280		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, TMEDA <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 15 min. CuI (1 eq), 15 min	CH <sub>2</sub> =CHCH <sub>2</sub> Br	A, RCH <sub>2</sub> C(CH <sub>3</sub> )=CHSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> + B, CH <sub>2</sub> =C(CH <sub>3</sub> )CH(R)SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> A: 9, B: 1, R = CH <sub>2</sub> CH=CH <sub>2</sub> (90)	280 280 280 280 280		
			C <sub>6</sub> H <sub>5</sub> C≡CCH(CH <sub>3</sub> )Br C <sub>6</sub> H <sub>5</sub> C≡CCHBrCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> CHO C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub> , CH <sub>3</sub> I	A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (89) A, R = CH(CH <sub>3</sub> )C≡CC <sub>6</sub> H <sub>5</sub> (50) A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (90) A, R = CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (80) A, R = CH <sub>3</sub> (75) A, R = CH <sub>3</sub> (70)	280 280 280 280 280		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	C <sub>6</sub> H <sub>5</sub> C≡CCH(CH <sub>3</sub> )Br C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub> <i>n</i> -C <sub>6</sub> H <sub>13</sub> Br (1.25 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (1.25 eq), 0°	No reaction A: 0, B: 1, R = CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (80) <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH(C <sub>6</sub> H <sub>13</sub> - <i>n</i> )C(CH <sub>3</sub> )=CH <sub>2</sub> (-)	280 280 316a		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	<i>n</i> -C <sub>6</sub> H <sub>13</sub> Br (1.25 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (1.25 eq), 0°	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH(C <sub>6</sub> H <sub>13</sub> - <i>n</i> )CH=CHCH <sub>3</sub> (-)	316a		
		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Cl <sup>-</sup> , CH <sub>2</sub> Cl <sub>2</sub> , 50% aqueous NaOH, room temperature, 6 hr <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -20°	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> C[CH=C(CH <sub>3</sub> ) <sub>2</sub> ]=CHC <sub>6</sub> H <sub>5</sub> (25) ( <i>E</i> )	158		
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>2</sub> =CHCH <sub>2</sub> Cl, -10°, 1 hr, 0°, 1 hr, 21°, 2 hr CH <sub>2</sub> CH(CH <sub>3</sub> )CH=CH <sub>2</sub> , room temperature	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CHRCH=C(CH <sub>3</sub> ) <sub>2</sub> A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (44) A, R = CH <sub>2</sub> C(OH)(CH <sub>3</sub> )CH=CH <sub>2</sub> (97)	332 326		
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF, -30°, 5 min	CH <sub>2</sub> =CHC(CH <sub>2</sub> Cl)=CH <sub>2</sub> , -30°, 2.5 hr	A, R = CH <sub>2</sub> C(CH=CH <sub>2</sub> )=CH <sub>2</sub> (93)	332		
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -10°	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Cl, -10°, 1.25 hr, 0°, 1 hr, 18°, 2 hr	A, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (-)	364		
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -20°	ClCH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OCOCH <sub>3</sub> , ( <i>E</i> ) -20°, 2.33 hr, 20°, 45 min, then KOH, H <sub>2</sub> O	A, R = CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OH (-)	365		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 1 hr	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> ( <i>E</i> ) C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	BrCH <sub>2</sub> C(CH <sub>3</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> , (-70°, 1 hr)	A, R = CH <sub>2</sub> C(CH <sub>3</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (83) ( <i>E</i> )	365	
				ClCH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OCOCH <sub>3</sub> , (-70°, 1 hr)	A, R = CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OCOCH <sub>3</sub> (83) ( <i>E</i> )	365	
				<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	CH <sub>3</sub> CH=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>	 (-)	594
				(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (1 eq)	 (-) + (CH <sub>3</sub> ) <sub>2</sub> C=CHCH(SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )COCH=C(CH <sub>3</sub> ) <sub>2</sub> (-) + (CH <sub>3</sub> ) <sub>2</sub> C=CHCH(SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (-)	148, 252	
				( <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>	 (-)	594	
 =CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>	 (-)			594			
C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>	 (-)			594			
<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), (CH <sub>3</sub> ) <sub>2</sub> NCHO, 0.25 hr, 25°	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , (2 eq)			 (-) +  (-)	148 148		
<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), (CH <sub>3</sub> ) <sub>2</sub> NCHO, 0.25 hr	 (2 eq)			A,  (-) + B,  (-)	148		
				A: 2, B: 3 (60)	148		

TABLE XXXII. SULFONES (Continued)

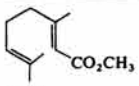
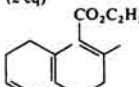
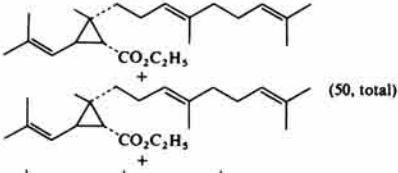
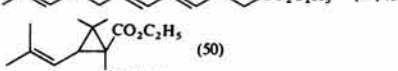
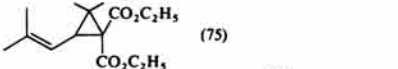
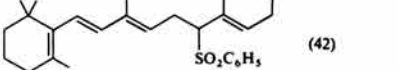
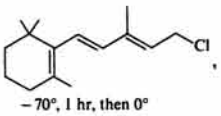
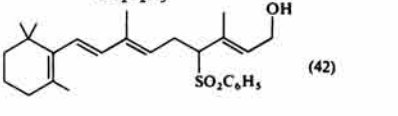
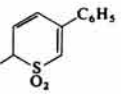
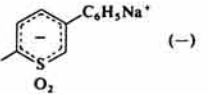
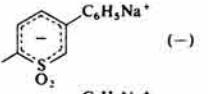
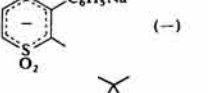
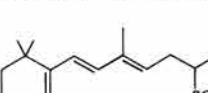
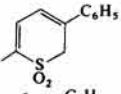
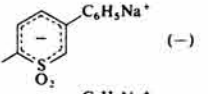
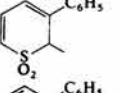
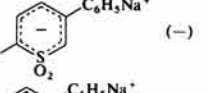
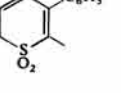
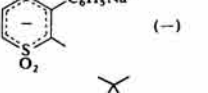
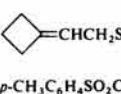
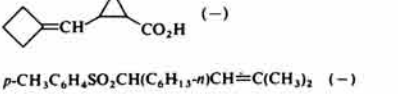
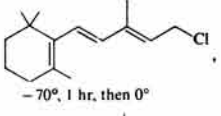
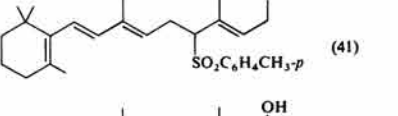
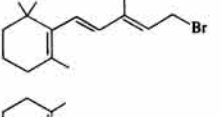
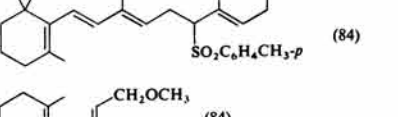
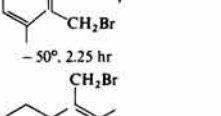
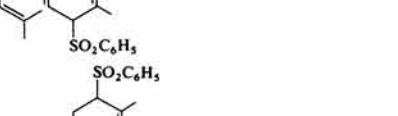
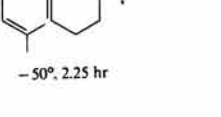
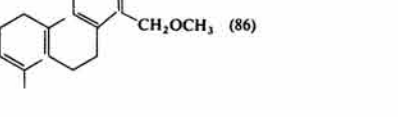
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>11</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), (CH <sub>3</sub> ) <sub>2</sub> NCHO 25°, 0.25 hr	 (2 eq)	A: 2, B: 3 (60)	148
			 (2 eq)		148
			(CH <sub>3</sub> ) <sub>2</sub> C=C(CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>		145
		C <sub>2</sub> H <sub>5</sub> MgBr, C <sub>6</sub> H <sub>6</sub> , CuCl	(CH <sub>3</sub> ) <sub>2</sub> C=C(CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>		145
		C <sub>2</sub> H <sub>5</sub> MgBr, C <sub>6</sub> H <sub>6</sub> , CuOAc			625
	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OH ( <i>E</i> )	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 30-40 min	 -70°, 1 hr, then 0°		625
C <sub>12</sub>		NaCH <sub>2</sub> S(O)CH <sub>3</sub> , CH <sub>3</sub> S(O)CH <sub>3</sub>	—	 (-)	71
			—	 (-)	71
			—	 (-)	71
			—	 (-)	594
		NaCH <sub>2</sub> S(O)CH <sub>3</sub> , CH <sub>3</sub> S(O)CH <sub>3</sub>	—	 (-)	316a
		NaCH <sub>2</sub> S(O)CH <sub>3</sub> , CH <sub>3</sub> S(O)CH <sub>3</sub>	—	 (-)	625
		NaCH <sub>2</sub> S(O)CH <sub>3</sub> , CH <sub>3</sub> S(O)CH <sub>3</sub>	—	 (-)	625
		<i>i</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>		316a
	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	<i>n</i> -C <sub>6</sub> H <sub>13</sub> Br (1.25 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (1.25 eq), 0°	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH(C <sub>6</sub> H <sub>13</sub> )CH=C(CH <sub>3</sub> ) <sub>2</sub> (-)	316a
249	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OH ( <i>E</i> )	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 30-40 min	 -70°, 1 hr, then 0°		625
					625
			LDA, THF, 70°, 25 min, base added to the substrates	 -50°, 2.25 hr	
	CH <sub>3</sub> OCH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -50°	 -50°, 2.25 hr		365

TABLE XXXII. SULFONES (Continued)

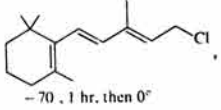
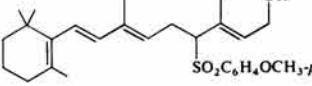
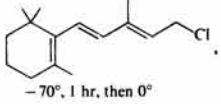
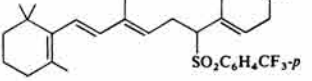
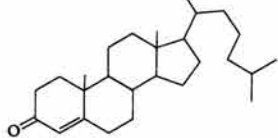
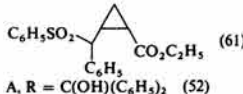
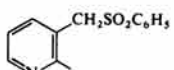
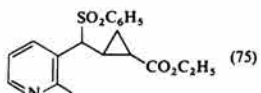
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>11</sub> (Contd.)	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OH (E)	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 30-40 min			(35-40)	625
	<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OH (E)	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 30-40 min			(3.5)	625
250	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CHSO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	Reflux, CH <sub>3</sub> OH	—	A, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> CH=CHCH <sub>2</sub> SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> CH <sub>2</sub> CH=CHSO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> A: 60, B: 40 (-)		555
C <sub>13</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.5 eq), THF, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 1 hr	D <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CRR'SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> A, R = R' = D (95)		55, 121
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.5 eq), THF, 25°, 1 hr, MgI <sub>2</sub> , ether, C <sub>6</sub> H <sub>6</sub> , 25°, 1 hr	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl (2.4 eq), reflux 22 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> Br (2.5 eq), reflux 24 hr C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> CH <sub>3</sub> (1 eq), reflux 4 hr CO <sub>2</sub>	A, R = R' = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (83) A, R = R' = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (72) A, R = H, R' = COC <sub>6</sub> H <sub>5</sub> (63) A, R = H, R' = CO <sub>2</sub> H (65)		55, 121
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, 25°, 1 hr, MgI <sub>2</sub> , ether, C <sub>6</sub> H <sub>6</sub> , 25°, 1 hr	CO <sub>2</sub>	A, R = H, R = CO <sub>2</sub> H (28)		53
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, 25°, 1 hr, MgI <sub>2</sub> , ether, C <sub>6</sub> H <sub>6</sub> , 25°, 1 hr	C <sub>3</sub> H <sub>7</sub> CHO	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> C(C <sub>6</sub> H <sub>5</sub> )=CHC <sub>2</sub> H <sub>5</sub> (8) + C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )CH(OH)C <sub>2</sub> H <sub>5</sub> (-) C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> C(C <sub>6</sub> H <sub>5</sub> )=CRR' (E) and (Z)		122
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, 25°, 1 hr, MgI <sub>2</sub> , ether, C <sub>6</sub> H <sub>6</sub> , 25°, 1 hr	C <sub>2</sub> H <sub>5</sub> CHO, reflux 2 hr	A, R = H, R' = C <sub>2</sub> H <sub>5</sub> (78)		122
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, 25°, 1 hr, MgI <sub>2</sub> , ether, C <sub>6</sub> H <sub>6</sub> , 25°, 1 hr	<i>n</i> -C <sub>3</sub> H <sub>7</sub> CHO, reflux 2 hr	A, R = H, R' = C <sub>3</sub> H <sub>7</sub> - <i>n</i> (70) (E) and (Z)		122
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, 25°, 1 hr, MgI <sub>2</sub> , ether, C <sub>6</sub> H <sub>6</sub> , 25°, 1 hr	C <sub>6</sub> H <sub>5</sub> CHO, reflux 2 hr	A, R = H, R' = C <sub>6</sub> H <sub>5</sub> (75) (Z)		122
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, 25°, 1 hr, MgI <sub>2</sub> , ether, C <sub>6</sub> H <sub>6</sub> , 25°, 1 hr	C <sub>2</sub> H <sub>5</sub> COCH <sub>3</sub> , reflux 2 hr	A, R = CH <sub>3</sub> , R' = C <sub>2</sub> H <sub>5</sub> (50) (E) and (Z)		122
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, 25°, 1 hr, MgI <sub>2</sub> , ether, C <sub>6</sub> H <sub>6</sub> , 25°, 1 hr	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHO, reflux 2 hr	A, R = H, R' = C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i> (72) (Z)		122
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, 25°, 1 hr, MgI <sub>2</sub> , ether, C <sub>6</sub> H <sub>6</sub> , 25°, 1 hr	<i>n</i> -C <sub>7</sub> H <sub>15</sub> CHO, reflux 2 hr	A, R = H, R' = C <sub>7</sub> H <sub>15</sub> - <i>n</i> (55)		122
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, 25°, 1 hr, MgI <sub>2</sub> , ether, C <sub>6</sub> H <sub>6</sub> , 25°, 1 hr	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> , reflux 2 hr	A, R = R' = C <sub>6</sub> H <sub>5</sub> (82)		122
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, 25°, 1 hr, MgI <sub>2</sub> , ether, C <sub>6</sub> H <sub>6</sub> , 25°, 1 hr	CH <sub>3</sub> COC <sub>6</sub> H <sub>13</sub> - <i>n</i> , reflux 2 hr	A, R = CH <sub>3</sub> , R' = C <sub>6</sub> H <sub>13</sub> - <i>n</i> (50) (E) and (Z)		122
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether	C <sub>6</sub> H <sub>5</sub> CHO		(65)	122
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 30 min, room temperature	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (1 eq), MgBr <sub>2</sub> (2 eq)	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> C(C <sub>6</sub> H <sub>5</sub> )=CHC <sub>2</sub> H <sub>5</sub> (E) and (Z)		472
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, 30 min, room temperature	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (1 eq), AlCl <sub>3</sub> (2 eq)	C <sub>6</sub> H <sub>5</sub> CHRSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> <i>erythro</i> : 23, <i>threo</i> : 77 (59)		453, 455
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>2</sub> CHCH <sub>3</sub> , room temperature, 4 hr	A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (50)		455
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>2</sub> CHC <sub>2</sub> H <sub>5</sub> , room temperature, 4 hr	A, R = CH <sub>2</sub> CH(OH)CH <sub>3</sub> (98)		326
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>2</sub> CHC <sub>2</sub> H <sub>5</sub> , room temperature, 4 hr	A, R = CH <sub>2</sub> CH(OH)C <sub>2</sub> H <sub>5</sub> (91)		326
		LDA, TMEDA, THF, -65°, 30 min	BrCH <sub>2</sub> CH=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , -60°, 30 min		(61)	253a
		<i>i</i> -C <sub>3</sub> H <sub>7</sub> MgBr (1 eq), THF, 30 min, room temperature	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (1 eq)	A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (52)		453, 455
		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Cl <sup>-</sup> , CH <sub>2</sub> Cl <sub>2</sub> , 50% aqueous NaOH, room temperature, 6 hr	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> C(C <sub>6</sub> H <sub>5</sub> )=CHC <sub>6</sub> H <sub>5</sub> (49) (Z)		158
		LDA, TMEDA, THF, -78°, then -20°, 1 hr	BrCH <sub>2</sub> CH=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , -78°, then -50°, 1 hr		(75)	253a

TABLE XXXII. SULFONES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>13</sub> (Cont'd.)		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>		(-)	594
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>		(-)	594
	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH(CO <sub>2</sub> CH <sub>3</sub> )SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	NaH, THF, 25°, 20-24 hr			(63)	261
					(80)	261
	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq), THF, room temperature	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Br	A,		147
			B,			
			C,			
				A: 54, B: 35, C: 11 (-)		
			(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Cl	A,	(-)	147
				B,		
				A: 75, B: 25 (-)		
					(-)	184
					(-)	
	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>		(-)	594
	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OH ( <i>E</i> )	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 30-40 min			(57)	625
C <sub>14</sub>	(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> SO <sub>2</sub>	KNH <sub>2</sub> (2 eq), NH <sub>3</sub> (liq), 15-20 min	NH <sub>4</sub> Cl	(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> SO <sub>2</sub> (81)		134
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl (1 eq), ether, then NH <sub>4</sub> Cl	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )SO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (86)		134
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl (2 eq), ether, then NH <sub>4</sub> Cl	[C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )] <sub>2</sub> SO <sub>2</sub> (77)		134
			C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (1 eq), then NH <sub>4</sub> Cl	C <sub>6</sub> H <sub>5</sub> CH(SO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (80-92)		134
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	LiAlH <sub>4</sub> , dioxane	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (56) <i>cis</i> : 1, <i>trans</i> : 1.8		418
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.2 eq), THF	CH <sub>3</sub> I CuCl <sub>2</sub> , room temperature	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (23) C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )SO <sub>2</sub> CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (-) C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> <i>cis</i> : 1, <i>trans</i> : 6 (39)		418 418	

TABLE XXXII. SULFONES (Continued)

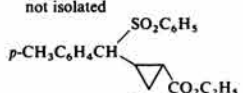
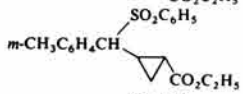
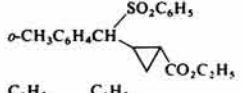

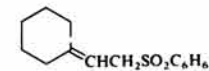
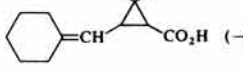
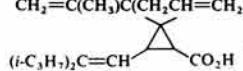
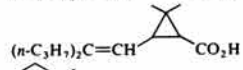
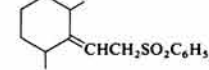
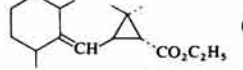
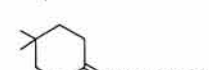
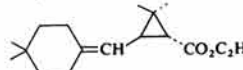
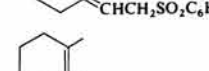
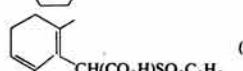
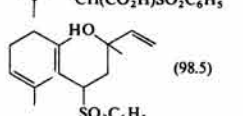
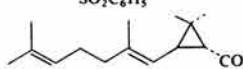
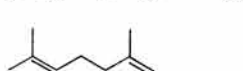
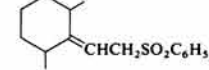
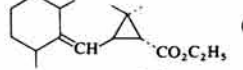
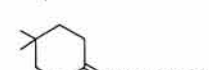
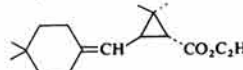
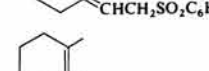
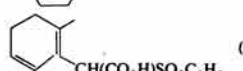
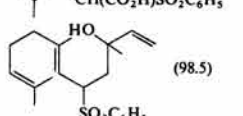
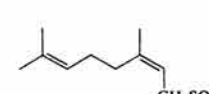
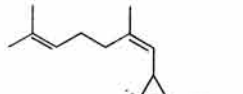
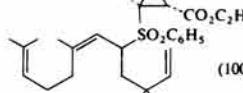
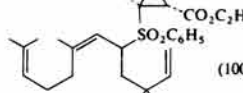
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>14</sub> (Contd.)	(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> SO <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.2 eq), THF, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 30 min, room temperature	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (1 eq), MgBr <sub>2</sub> (2 eq), H <sup>+</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (42)	455
		<i>i</i> -C <sub>3</sub> H <sub>7</sub> MgBr (2 eq), THF, 30 min, room temperature	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (1 eq)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (56)	455
	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub> MgBr (2 eq), or <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, MgBr <sub>2</sub> KNH <sub>2</sub> , NH <sub>3</sub> (liq)	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (42-56)	453
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 30 min, room temperature	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (1 eq), AlCl <sub>3</sub> (2 eq)	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CHRC <sub>6</sub> H <sub>5</sub> A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (91) A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (36)	586 455
		C <sub>2</sub> H <sub>5</sub> MgBr, C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	CH <sub>3</sub> ONH <sub>2</sub>	A, R = NH <sub>2</sub> (-) not isolated	403
	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	LDA, TMEDA, THF, -65°, 30 min	BrCH <sub>2</sub> CH=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , -60°, 30 min	 (78)	253a
	<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	LDA, TMEDA, THF, -65°, 30 min	BrCH <sub>2</sub> CH=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , -60°, 30 min	 (72)	253a
	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	LDA, TMEDA, THF, -65°, 30 min	BrCH <sub>2</sub> CH=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , -60°, 30 min	 (77)	253a
	C <sub>6</sub> H <sub>5</sub> CHBrSO <sub>2</sub> CHBrC <sub>6</sub> H <sub>5</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>2</sub> Cl <sub>2</sub>	—	 (70)	361
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>	 (-)	594
C <sub>15</sub>	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(CH <sub>2</sub> CH=CH <sub>2</sub> )SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 15 min, CuI (1 eq), 15 min	CH <sub>2</sub> =CHCH <sub>2</sub> Br	CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=C(CH <sub>2</sub> CH=CH <sub>2</sub> )SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (71)	280
				CH <sub>2</sub> =C(CH <sub>3</sub> )C(CH <sub>2</sub> CH=CH <sub>2</sub> )SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (6)	
	<i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>	 (-)	594
	<i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>	 (-)	594
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	 (-)	594
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	 (-)	594
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	CO <sub>2</sub>	 (-)	587
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>2</sub> C(CH <sub>3</sub> )CH=CH <sub>2</sub>	 (98.5)	326
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), (CH <sub>3</sub> ) <sub>2</sub> NCHO, 25°, 0.25 hr	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (2 eq)	 (-)	148
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), (CH <sub>3</sub> ) <sub>2</sub> NCHO, 25°, 0.25 hr	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (2 eq)	 (-)	148
C <sub>16</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	 (-)	594
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	 (-)	594
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	CO <sub>2</sub>	 (-)	587
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>2</sub> C(CH <sub>3</sub> )CH=CH <sub>2</sub>	 (98.5)	326
C <sub>17</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), (CH <sub>3</sub> ) <sub>2</sub> NCHO, 25°, 0.25 hr	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (2 eq)	 (-)	148
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), (CH <sub>3</sub> ) <sub>2</sub> NCHO, 25°, 0.25 hr	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (2 eq)	 (-)	148
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>2</sub> C(CH <sub>3</sub> )CH=CH <sub>2</sub>	 (100)	326
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF-ethcr. 2:8, room temperature, 30 min	D <sub>2</sub> O	( <i>π</i> -C <sub>5</sub> H <sub>5</sub> )Fe(C <sub>2</sub> H <sub>4</sub> - <i>π</i> )CRR'SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> A, R = R' = D (95)	400

TABLE XXXII. SULFONES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>17</sub> (Contd.)	( $\pi$ -C <sub>5</sub> H <sub>5</sub> )Fe(C <sub>5</sub> H <sub>4</sub> - $\pi$ )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF-ether, 2:8, room temperature, 30 min	CH <sub>3</sub> I, reflux, 30 min <i>n</i> -C <sub>4</sub> H <sub>9</sub> Br, reflux, 30 min C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl, reflux, 30 min	A, R = R' = CH <sub>3</sub> (74) A, R = H, R' = C <sub>6</sub> H <sub>5</sub> - $\pi$ (63) A, R = H, R' = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (58)	400 400 400
			ClCH <sub>2</sub> CH <sub>2</sub> Cl, reflux, 6 hr C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl, reflux, 6 hr	A, R = R' = (CH <sub>2</sub> ) <sub>2</sub> (89) ( $\pi$ -C <sub>5</sub> H <sub>5</sub> )Fe(C <sub>5</sub> H <sub>4</sub> - $\pi$ )C(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )=CHC <sub>6</sub> H <sub>5</sub> (E) and (Z) (74)	400 400
256		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), DABCO, THF, -15°, 20 min	CH <sub>3</sub> I		219
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), DABCO, THF, -15°, 20 min	CH <sub>3</sub> I		219
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 4:1, -20°			319
					319
	( <i>i</i> -C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>	( <i>i</i> -C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> ) <sub>2</sub> C=CH  (-)	594
C <sub>18</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>	(-)	594
C <sub>19</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, (CH <sub>3</sub> ) <sub>2</sub> NCHO-THF, 1:1, -78°, 10 min	ClCH <sub>2</sub> --CH <sub>2</sub> O <sub>2</sub> CCH <sub>3</sub> , -40°	(84)	305
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -40°	BrCH <sub>2</sub> CH=CHCHBrCH <sub>3</sub> , -50°, 5 hr	(-)	366
		NaOH, 0°, 10 min	ClCH <sub>2</sub> --CH <sub>2</sub> O <sub>2</sub> CCH <sub>3</sub> , 0°, 30 min, then room temperature, 16 hr	(35)	305
				(54)	
				(04)	
		CH <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub> , NaOH, 0°, 10 min	ClCH <sub>2</sub> --CH <sub>2</sub> Cl	(-)	324

TABLE XXXII. SULFONES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>19</sub> (Contd.)		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -12°	$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{O}_2\text{CCH}_3$ , -50°, then room temperature, 20 min		306
C <sub>20</sub>		KOH, CCl <sub>4</sub> , room temperature	—		358
C <sub>21</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (2 eq), THF	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , then OH <sup>-</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CH  (-)	594
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -10°, 5 min	$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{O}_2\text{CCH}_3$ , 5°, 25 min		306
		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> OH <sup>-</sup> , CH <sub>3</sub> CN	CH <sub>2</sub> =C(CH <sub>3</sub> )CH=CHSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>		365
		NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, -5°, 15 min	$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{O}_2\text{CCH}_3$ , ( <i>E</i> )		
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq), THF, -65° to -60°	BrCH <sub>2</sub> C(CH <sub>3</sub> )=CHCO <sub>2</sub> CH <sub>3</sub>	A, R = CH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> O <sub>2</sub> CCH <sub>3</sub> (73)	306
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -73°	$\text{ClCH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$ , ( <i>E</i> ) -73°, 4 hr, then -30°, 2 hr	A, R = CH <sub>2</sub> C(CH <sub>3</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (98)	184
				A, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> Cl (90)	364
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -50°	$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CHCH}(\text{OC}_2\text{H}_5)_2$ , ( <i>E</i> ) -50°, 30 min, -20°, 2 hr, 0°, 3 hr	A, R = CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (72)	365
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -30°	$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{O}_2\text{CCH}_3$ , ( <i>E</i> ) -30°, 5 hr	A, R = CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OCOCH <sub>3</sub> (65)	365
			$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OCH}_3$ , ( <i>E</i> ) -30°, 2 hr	A, R = CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OCH <sub>3</sub> (85)	365
			$\text{ClCH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$ (0.5 eq) ( <i>E</i> )	A, R =	364,365
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -30°, 10 min	CH <sub>2</sub> =CHC(CH <sub>2</sub> Cl)=CH <sub>2</sub> , -30°, 5 hr	A, R = CH <sub>2</sub> C(CH=CH <sub>2</sub> )=CH <sub>2</sub> (81)	332
			$\text{ClCH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$ ( <i>E</i> )	A, R =	365
			$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{SO}_2\text{C}_6\text{H}_5$ , ( <i>E</i> ) -30°, 3.5 hr	A, R = CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (89.5)	365
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>2</sub> C(CH <sub>3</sub> )CH=CH <sub>2</sub> 	A, R = CH <sub>2</sub> C(CH <sub>3</sub> )(OH)CH=CH <sub>2</sub> (93)	326
		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> OH <sup>-</sup> , CH <sub>3</sub> CN, room temperature, 2 hr	CH <sub>2</sub> =CHC(CH <sub>3</sub> )=CHSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	A, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (68) ( <i>E</i> )	364
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), (CH <sub>3</sub> ) <sub>2</sub> NCHO, 25°, 0.25 hr	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (2 eq)		148

TABLE XXXII. SULFONES (Continued)

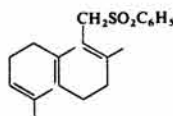
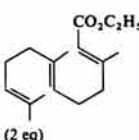
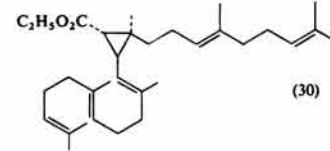
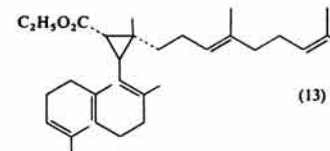
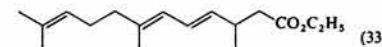
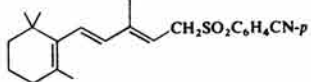
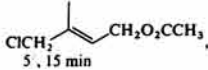
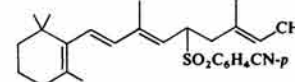
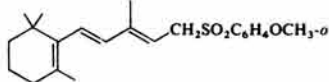
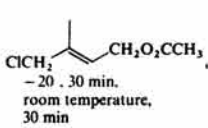
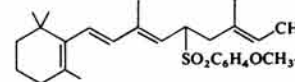
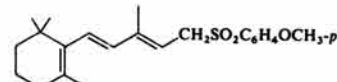
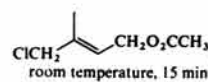
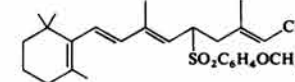
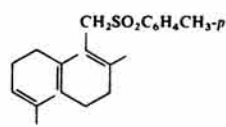
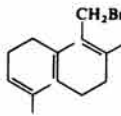
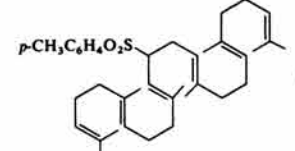
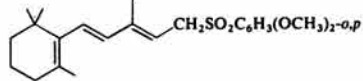
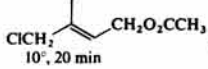
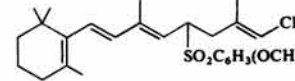
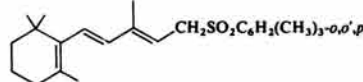
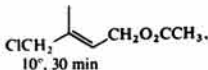
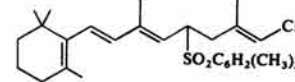
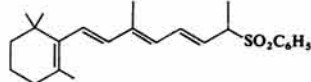
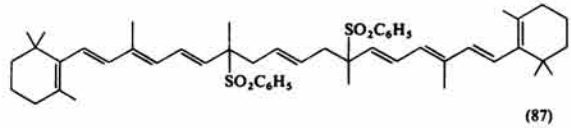
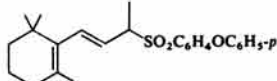
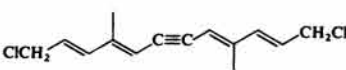
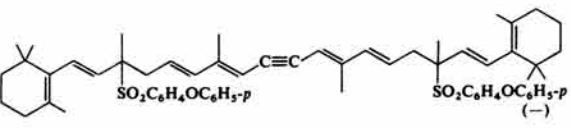
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>21</sub> (Contd.)		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), (CH <sub>3</sub> ) <sub>2</sub> NCHO, 25°, 0.25 hr	 (2 eq)	 (30)	148
260				 (13)	
				 (33)	
C <sub>22</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -15°, 7 min	 5, 15 min	 (44)	306
		NaCH <sub>2</sub> SOCH <sub>3</sub> , THF, -10°, 4 min	 -20, 30 min, room temperature, 30 min	 (66)	306
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -20°, 5 min	 room temperature, 15 min	 (50)	306
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 4:1, -20°		 (86)	319
C <sub>23</sub>		NaCH <sub>2</sub> SOCH <sub>3</sub> , THF, -30°, 5 min	 10°, 20 min	 (72)	306
C <sub>24</sub>		NaH, (CH <sub>3</sub> ) <sub>2</sub> NCHO, 0°, 10 min	 10°, 30 min	 (78)	306
261		CH <sub>3</sub> ONa, THF, -10°	BrCH <sub>2</sub> CH=CHCH <sub>2</sub> Br, -10°, 10 hr	 (87)	366
C <sub>25</sub>		CH <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub> , NaOH, 0°, 10 min		 (-)	325



TABLE XXXII. SULFONES (Continued)

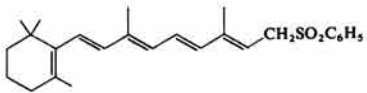
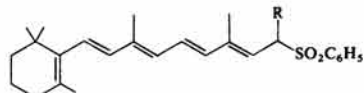
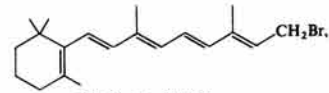
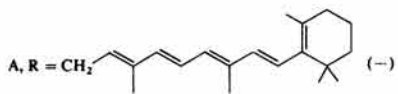
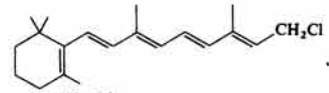
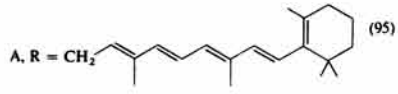
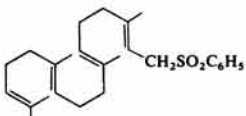
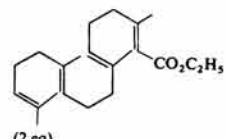
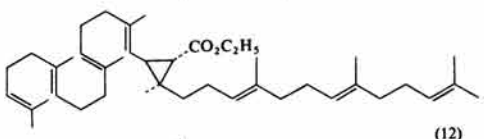
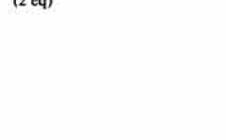
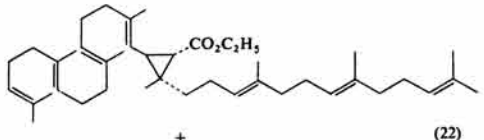

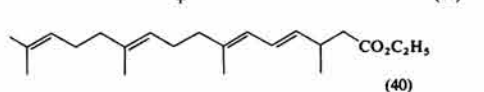
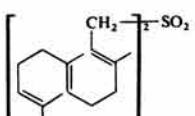
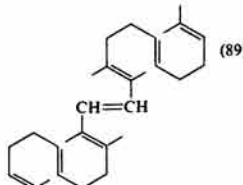
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
262		$\text{CH}_3\text{OK}$ , ether- $[[(\text{CH}_3)_2\text{N}]_3\text{PO}$ , 1:1, $-20^\circ$	$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CHCO}_2\text{CH}_3$ , $-20^\circ$ , 2.5 hr	 A, R = $\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCO}_2\text{CH}_3$ (71) A, R = $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$ (98)	365 364
		$t\text{-C}_4\text{H}_9\text{OK}$ , THF, $-70^\circ$	$\text{ClCH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$ , (E) $-70^\circ$ , 5 hr	A, R = $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{OC}_4\text{H}_9\text{-}t$ (-)	364
		$t\text{-C}_4\text{H}_9\text{OK}$ , THF, $-30^\circ$ , 10 min	$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{SO}_2\text{C}_6\text{H}_5$ , (E) $-71^\circ$ , 15 hr, then $-50^\circ$ , 3.75 hr	A, R = $\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{SO}_2\text{C}_6\text{H}_5$ (84)	365
		$t\text{-C}_4\text{H}_9\text{OK}$ , THF, $-25^\circ$	$\text{ClCH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{SO}_2\text{C}_6\text{H}_5$ , (E) $-30^\circ$ , 3.5 hr	A, R = $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{SO}_2\text{C}_6\text{H}_5$ (70)	364
		$t\text{-C}_4\text{H}_9\text{OK}$ , THF, $0^\circ$ , 6 min	$\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{O}_2\text{CCH}_3$ , (E) $-15^\circ$ , 7.5 hr, then $-70^\circ$ , 16 hr $18^\circ$ , 3 hr	A, R = $\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{O}_2\text{CCH}_3$ (67)	365
		$t\text{-C}_4\text{H}_9\text{OK}$ , THF, $14^\circ$	 $-30^\circ$ , 10 min, $5^\circ$ , 1.5 hr	 A, R = $\text{CH}_2$ (-)	322
		$t\text{-C}_4\text{H}_9\text{OK}$ , THF, $-30^\circ$	 $-10^\circ$ , 3 hr	 A, R = $\text{CH}_2$ (95)	322
263		$t\text{-C}_4\text{H}_9\text{OK}$ (3 eq), $(\text{CH}_3)_2\text{NCHO}$ , $25^\circ$ , 0.25 hr	 (2 eq)	 (12)	148, 328
			 (22)	 (22)	
			 (40)	 (40)	
30		$\text{KOH}$ , $\text{CCl}_4$ , room temperature	—	 (89)	358

TABLE XXXII. SULFONES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>32</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -30°	 -15°, 2 hr, then 0°, 10 hr	 364	
C <sub>37</sub>		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -70°	ClCH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> - <i>t</i> , ( <i>E</i> ) -70°, 19 hr	 A, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> - <i>t</i> (72) 365	
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -30°	 -30°, 3 hr, then 0°, 16 hr	 A, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> OC <sub>4</sub> H <sub>9</sub> - <i>t</i> (-) 365	
C <sub>40</sub>		LDA, THF, 0°	I <sub>2</sub> or Br <sub>2</sub>	 (24) 358	

TABLE XXXIII. SULFONIC ESTERS

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>13</sub>	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )SO <sub>3</sub> CH <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 15 min	CH <sub>3</sub> I, -78°, 1-2 hr	C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub> SO <sub>3</sub> CH <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i> (89.8)	54
			<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br, -78°, 12 hr	C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )(C <sub>3</sub> H <sub>7</sub> - <i>n</i> )SO <sub>3</sub> CH <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i> (-)	54

TABLE XXXIV. SULFOXIDES



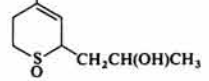
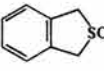
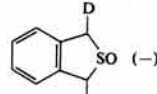
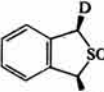
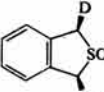
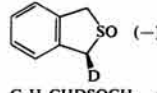

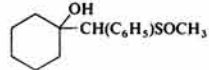
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>4</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> SOCH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, room temperature, 1 hr	—	A, CH <sub>2</sub> =CHCH <sub>2</sub> SOCH <sub>3</sub> + B, CH <sub>3</sub> CH=CHSOCH <sub>3</sub> A: 20, B: 80 (—) A: 43, B: 57 (—) A: 17, B: 83 (—)	522 522 522
	CH <sub>3</sub> CH=CHSOCH <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, reflux, 18 hr <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, room temperature, 1 hr (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, reflux, 18 hr	— — —	A: 33, B: 67 (—)	522
C <sub>6</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -50°, then -20°, 2 hr	CH <sub>3</sub> CHCH <sub>2</sub> 	(—) 	481
C <sub>7</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> CH=CHSOCH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH, room temperature, 4 hr	—	A, <i>n</i> -C <sub>3</sub> H <sub>7</sub> CH=CHCH <sub>2</sub> SOCH <sub>3</sub> + B, <i>n</i> -C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> CH=CHSOCH <sub>3</sub> A: 96, B: 4 (—)	522
C <sub>8</sub>		NaOD, D <sub>2</sub> O	HCl	 (—)	471
		CH <sub>3</sub> Li (2.2 eq), THF, 0°	DCI	(1.5 D) (—)	471
		CH <sub>3</sub> Li (1.1 eq), THF, 0°	HCl	 (—)	471
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SOCH <sub>3</sub>	NaOD, D <sub>2</sub> O	—	C <sub>6</sub> H <sub>5</sub> CHDSOCH <sub>3</sub> (—)	341, 607
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OLi, CD <sub>3</sub> SOCD <sub>3</sub> , 24° <i>t</i> -C <sub>4</sub> H <sub>9</sub> OLi, C <sub>6</sub> H <sub>6</sub> , 24° <i>t</i> -C <sub>4</sub> H <sub>9</sub> OLi, THF, -60° -20° 24°	D <sub>2</sub> O D <sub>2</sub> O D <sub>2</sub> O	RS: 1.7, SS: 1 (—) RS: 0.11, SS: 1 (—) RS: 0.065, SS: 1 (—) RS: 0.080, SS: 1 (—) RS: 0.13, SS: 1 (—)	51 51 51 51 51
C <sub>9</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1.1 eq), THF, -70°	D <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CHDSOCH <sub>3</sub> (—)	292, 516
			CH <sub>3</sub> I CH <sub>3</sub> COCH <sub>3</sub>	<i>threo</i> C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )SOCH <sub>3</sub> (—) C <sub>6</sub> H <sub>5</sub> CH(SOCH <sub>3</sub> )C(OH)(CH <sub>3</sub> ) <sub>2</sub> <i>threo</i> C <sub>6</sub> H <sub>5</sub> CH(CO <sub>2</sub> H)SOCH <sub>3</sub> (50)	290, 292 292 292
		CH <sub>3</sub> Li, THF, -60°, 1 min	D <sub>2</sub> O	<i>threo</i> C <sub>6</sub> H <sub>5</sub> CHDSOCH <sub>3</sub> (85)	287
			CH <sub>3</sub> I CH <sub>3</sub> COCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )SOCH <sub>3</sub> (76) RS: 15, SS: 1 C <sub>6</sub> H <sub>5</sub> CH(SOCH <sub>3</sub> )C(OH)(CH <sub>3</sub> ) <sub>2</sub> (75)	287, 289 287
				 (72)	287
		CH <sub>3</sub> Li, LiCl (1.1 eq), THF, -60°, 1 min	D <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CHDSOCH <sub>3</sub> RS/SR: 1, RR/SS: 15 (—)	288
		CH <sub>3</sub> Li, LiBr (1.1 eq), THF, -60°, 1 min	D <sub>2</sub> O	RS/SR: 1, RR/SS: 3 (—)	288
		CH <sub>3</sub> Li, LiCl (1.1 eq), THF, -60°, 1 min	CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )SOCH <sub>3</sub> SR/RS: 15, RR/SS: 1 (—)	288
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -50°	CH <sub>3</sub> I	A, CH <sub>2</sub> =CHCHR <sub>2</sub> SOCH <sub>3</sub> + B, RCH <sub>2</sub> CH=CHSOCH <sub>3</sub> A: 1, B: 0, R = CH <sub>3</sub> (—) A: 5.6, B: 1, R = CH <sub>3</sub> (—) A: 2.9, B: 1, R = C <sub>2</sub> H <sub>5</sub> (—) A: 1.3, B: 1, R = CH <sub>2</sub> CH=CH <sub>2</sub> (—)	308 225 225 225
		LDA, THF, -60°, 15 min	CH <sub>3</sub> I C <sub>2</sub> H <sub>5</sub> I CH <sub>2</sub> =CHCH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> CD(CH <sub>3</sub> )SOCH <sub>3</sub> RS/SR: 1, RR/SS: 2 (—) C <sub>6</sub> H <sub>5</sub> CH=CHC(OH)(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> C(CH <sub>3</sub> )=CHSOCH <sub>3</sub> (42)	390 166
C <sub>10</sub>	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )SOCH <sub>3</sub> RS and SR	NaOD, D <sub>2</sub> O, 50°	—		
	CH <sub>2</sub> =C=CHSOCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> CH <sub>2</sub> =CHCH(CH <sub>3</sub> )SOCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	(CH <sub>3</sub> CuCH <sub>3</sub> )Li, THF-ether, 1:1, -20°, 20 min LDA, THF, -60°, 15 min	C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> I	A, CH <sub>2</sub> =CHCR(CH <sub>3</sub> )SOCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> + B, RCH <sub>2</sub> CH=C(CH <sub>3</sub> )SOCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> A: 2.6, B: 1, R = CH <sub>3</sub> (—) A: 2.4, B: 1, R = C <sub>2</sub> H <sub>5</sub> (—) A: 1.1, B: 1, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (—) A: 1, B: 0, R = (CH <sub>2</sub> ) <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (—)	271 271 271 271
	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SOCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	LDA, THF, -60°, 15 min	CH <sub>3</sub> I C <sub>2</sub> H <sub>5</sub> I (CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Br (CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> CH <sub>2</sub> I CH <sub>3</sub> I	A, CH <sub>2</sub> =C(CH <sub>3</sub> )CHR <sub>2</sub> SOCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> + B, RCH <sub>2</sub> C(CH <sub>3</sub> )=CHSOCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> A: 10, B: 1, R = CH <sub>3</sub> (—) A: 2.5, B: 1, R = C <sub>6</sub> H <sub>13</sub> - <i>n</i> (—) A: 2, B: 1, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (—) A: 2, B: 1, R = (CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (—)	271 271 271 271
			<i>n</i> -C <sub>6</sub> H <sub>13</sub> I (CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Br <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> I	A: 2, B: 1, R = (CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (—)	271

TABLE XXXIV. SULFOXIDES (Continued)

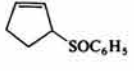
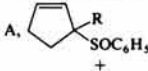
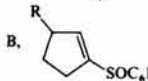
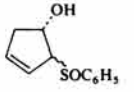
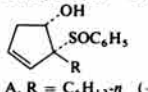

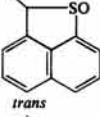
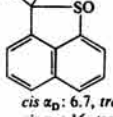
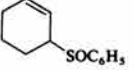
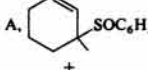
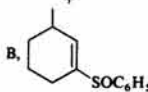
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>10</sub>	CH <sub>3</sub> CH=CHCH <sub>2</sub> SOC <sub>6</sub> H <sub>5</sub>	LDA, THF, -60°, 15 min	CH <sub>3</sub> I	A, CH <sub>3</sub> CH=CHCHRSOC <sub>6</sub> H <sub>5</sub> + B, R(CH <sub>3</sub> )CHCH=CHSOC <sub>6</sub> H <sub>5</sub> A: 10, B: 1, R = CH <sub>3</sub> (-) A: 6.7, B: 1, R = C <sub>2</sub> H <sub>5</sub> (-)	225 225
C <sub>11</sub>	CH <sub>3</sub> CH=C=CHSOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	(CH <sub>3</sub> CuCH <sub>3</sub> )Li	C <sub>2</sub> H <sub>5</sub> I NH <sub>4</sub> Cl	CH <sub>3</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> SOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> <i>cis</i> : 34, <i>trans</i> : 66 (69)	166
		LDA, THF, -60°, 15 min	CH <sub>3</sub> I	A,  + B, 	225 225 225
		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NLi, THF, -40°, 30 min	C <sub>2</sub> H <sub>5</sub> I CH <sub>2</sub> =CHCH <sub>2</sub> Br  n-C <sub>6</sub> H <sub>13</sub> I	 + A, R = C <sub>6</sub> H <sub>13</sub> - <i>n</i> (-) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-) A, R = CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (-)	140 140 140
		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NLi, THF, -40°, 30 min	n-C <sub>6</sub> H <sub>13</sub> I	A, R = (CH <sub>2</sub> ) <sub>6</sub> -O-C <sub>6</sub> H <sub>5</sub> (-)	140
	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SOC <sub>6</sub> H <sub>5</sub>	LDA, THF, -60°, 15 min	I(CH <sub>2</sub> ) <sub>6</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i> BrCH <sub>2</sub> C≡C(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i> n-C <sub>6</sub> H <sub>13</sub> I	A, R = (CH <sub>2</sub> ) <sub>6</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i> (-) A, R = CH <sub>2</sub> C≡C(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i> A, (CH <sub>3</sub> ) <sub>2</sub> C=CHCH(C <sub>6</sub> H <sub>13</sub> - <i>n</i> )SOC <sub>6</sub> H <sub>5</sub> + B, n-C <sub>6</sub> H <sub>13</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH=CHSOC <sub>6</sub> H <sub>5</sub> A: 10, B: 1 (-)	140 140 140
	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	n-C <sub>4</sub> H <sub>9</sub> Li, THF, -40°	C <sub>2</sub> H <sub>5</sub> I  n-C <sub>4</sub> H <sub>9</sub> I	CH <sub>2</sub> =C(CH <sub>3</sub> )CHRSOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> A, R = C <sub>2</sub> H <sub>5</sub> (-) A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> (90)	225 307 307
		n-C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 15 min	CH <sub>3</sub> I CH <sub>2</sub> =CHCH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CHO	A, R = CH <sub>3</sub> (98) A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (40) RCH <sub>2</sub> C(CH <sub>3</sub> )=CHSOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (36)	280 280 280
		CuI (1 eq) added, 15 min	C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> I CH <sub>2</sub> =CHCH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub>	A, R = C(OH)C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (20) CH <sub>2</sub> =C(CH <sub>3</sub> )CH(CH <sub>3</sub> )SOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (60) CH <sub>2</sub> =C(CH <sub>3</sub> )CH(CH <sub>2</sub> CH=CH <sub>2</sub> )SOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (20) C <sub>6</sub> H <sub>5</sub> CH=CHC(OH)(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> C(CH <sub>3</sub> )=CHSOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (-)	280 280 280
		CH <sub>3</sub> Li (1 eq), THF, -70°, 30 min, CuI (1 eq), -20°, 5 min, CH <sub>3</sub> Li (1 eq), -20° CH <sub>3</sub> Li, THF, -60°, 1 min	C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> C(CH <sub>3</sub> )=CHSOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (traces) C <sub>6</sub> H <sub>5</sub> CH=CHC(OH)(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> C(CH <sub>3</sub> )=CHSOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (20)	166
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SOC <sub>4</sub> H <sub>9</sub> - <i>t</i> S	CH <sub>3</sub> Li, THF, -60°, 1 min	D <sub>2</sub> O CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> CHDSOC <sub>4</sub> H <sub>9</sub> - <i>t</i> (90) RS: 99, SS: 1	287 287
	C <sub>6</sub> H <sub>5</sub> CHDSOC <sub>4</sub> H <sub>9</sub> - <i>t</i> RR, SS RS, SR SS	n-C <sub>4</sub> H <sub>9</sub> Li, THF, -70°	CH <sub>3</sub> COCH <sub>3</sub> H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH[C(OH)(CH <sub>3</sub> ) <sub>2</sub> ]SOC <sub>4</sub> H <sub>9</sub> - <i>t</i> (77) C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SOC <sub>4</sub> H <sub>9</sub> - <i>t</i> (-)	297 291
		CH <sub>3</sub> Li, THF, -60°	H <sub>2</sub> O CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> CHDSOC <sub>4</sub> H <sub>9</sub> - <i>t</i> (-) A, C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )SOC <sub>4</sub> H <sub>9</sub> - <i>t</i> + B, C <sub>6</sub> H <sub>5</sub> CD(CH <sub>3</sub> )SOC <sub>4</sub> H <sub>9</sub> - <i>t</i> A: 97.9, B: 2.1 (-)	291 287
C <sub>12</sub>	 <i>trans</i> <i>cis</i>	CH <sub>3</sub> ONa, CH <sub>3</sub> OD	-	 <i>cis</i> α <sub>D</sub> : 6.7, <i>trans</i> α <sub>D</sub> : 1 (-) <i>cis</i> α <sub>D</sub> : 16, <i>trans</i> α <sub>D</sub> : 1 (-)	406 406
		LDA, THF, -60°, 15 min	CH <sub>3</sub> I	A,  + B, 	225

TABLE XXXIV. SULFOXIDES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>11</sub> (Contd.)	 $n\text{-C}_8\text{H}_{17}\text{CH}=\text{CHCH}_2\text{SOCH}_3$	$sec\text{-C}_4\text{H}_9\text{Li}$ , THF, $-40^\circ$	$\text{BrCH}_2\text{C}(\text{CH}_3)=\text{CHCO}_2\text{CH}_3$	 $n\text{-C}_8\text{H}_{17}\text{CD}=\text{CHCD}_2\text{SOCH}_3$ (-)	142
C <sub>13</sub>	$\text{C}_6\text{H}_5\text{CH}_2\text{SOCH}_2\text{C}_6\text{H}_5$	$t\text{-C}_4\text{H}_9\text{OK}$ , $t\text{-C}_4\text{H}_9\text{OD}$ , room temperature, 24 hr $\text{CH}_3\text{Li}$ , THF, $-60^\circ$ , 1 min	$\text{D}_2\text{O}$ $\text{CH}_3\text{I}$	$\text{C}_6\text{H}_5\text{CHRSOC}_6\text{H}_5$ A, R = D (80) A, R = $\text{CH}_3$ (79)	287 287
270	$p\text{-ClC}_6\text{H}_4\text{SOCH}_2\text{C}_6\text{H}_5$	$n\text{-C}_4\text{H}_9\text{Li}$ , ether, 15 min LICA, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ , $0^\circ$ , 1 hr	 $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3$ $i\text{-C}_3\text{H}_7\text{I}$ , $20^\circ$ , 20 hr	A, R =  (85)	287
			$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ , $20^\circ$ , 1 hr $(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_2)_2\text{CH}(\text{CH}_3)(\text{CH}_2)_2\text{I}$ , $20^\circ$ , 3 hr	A, R = $\text{CH}_2\text{C}_6\text{H}_5$ (-) A, R = $(\text{CH}_2)_2\text{CH}(\text{CH}_3)(\text{CH}_2)_2\text{CH}=\text{C}(\text{CH}_3)_2$ (-)	141 141
			 $20^\circ$ , 4 hr	A, R =  (-)	141
			 $20^\circ$ , 1 hr	A, R =  (-)	141
			$\text{D}_2\text{O}$	$\text{C}_6\text{H}_5\text{CD}_2\text{SOC}_6\text{H}_5$ (95)	55
		$n\text{-C}_4\text{H}_9\text{Li}$ (2.6 eq), THF, $n\text{-C}_4\text{H}_9\text{I}$ , $0^\circ$ , 15 min NaOD, $\text{D}_2\text{O}$ , dioxane	-	$p\text{-ClC}_6\text{H}_4\text{SOCHDC}_6\text{H}_5$ (-) <i>gauche</i> proton exchanged faster	517
	 $n\text{-C}_9\text{H}_{19}\text{CH}_2\text{CH}=\text{CHSOCH}_3$	LDA, TMEDA, THF, $-78^\circ$ then $-20^\circ$ , 1 hr $t\text{-C}_4\text{H}_9\text{OK}$ , $t\text{-C}_4\text{H}_9\text{OH}$ , room temperature, 5 hr	$\text{BrCH}_2\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ , $-78^\circ$ , then $-50^\circ$ , 1 hr	 A, $n\text{-C}_9\text{H}_{19}\text{CH}=\text{CHCH}_2\text{SOCH}_3$ + B, $n\text{-C}_9\text{H}_{19}\text{CH}_2\text{CH}=\text{CHSOCH}_3$ A: 96, B: 4 (-)	253a 522
		NaOD, $\text{D}_2\text{O}$ , room temperature, 66 hr 2 wk	-	A, $n\text{-C}_9\text{H}_{19}\text{CH}=\text{CHCD}_2\text{SOCH}_3$ + B, $n\text{-C}_{10}\text{H}_{21}\text{CH}=\text{CHSOCH}_3$ A: 2, B: 8 (-) A: 65, B: 35 (-)	521 521
	$n\text{-C}_9\text{H}_{19}\text{CH}=\text{CHCH}_2\text{SOCH}_3$	$t\text{-C}_4\text{H}_9\text{OK}$ , $t\text{-C}_4\text{H}_9\text{OH}$ , room temperature, 5 hr	-	A, $n\text{-C}_9\text{H}_{19}\text{CH}=\text{CHCH}_2\text{SOCH}_3$ + B, $n\text{-C}_{10}\text{H}_{21}\text{CH}=\text{CHSOCH}_3$ A: 96, B: 4 (-)	523 521
271	 $\text{C}_6\text{H}_5\text{CH}_2\text{SOCH}_2\text{C}_6\text{H}_5$	$n\text{-C}_4\text{H}_9\text{Li}$ (2 eq), THF, $-78^\circ$ , 30 min $n\text{-C}_4\text{H}_9\text{Li}$ (2 eq), THF, $25^\circ$ , 30 min $\text{KNH}_2$ , $\text{NH}_3$ (liq) $t\text{-C}_4\text{H}_9\text{OK}$ , $(\text{CH}_3)_2\text{NCHO}$ , $80^\circ$ , 20 hr	 $\text{D}_2\text{O}$	 $\text{C}_6\text{H}_5\text{CHDSOCHDC}_6\text{H}_5$ (-)	141
			$\text{H}^+$	$\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$ (61)	455
			$\text{H}^+$	$\text{C}_6\text{H}_5\text{CH}_2\text{SOCH}_2\text{C}_6\text{H}_5$ (-) $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$ (50) <i>cis</i> : 1, <i>trans</i> : 12	454 598, 599
			$\text{CH}_3\text{OH}$	 (-)	154
				$p\text{-CH}_3\text{C}_6\text{H}_4\text{SOCH}_2\text{CH}=\text{CHC}_6\text{H}_5$ (-) $p\text{-CH}_3\text{C}_6\text{H}_4\text{SOCH}_2\text{CH}=\text{CHC}_6\text{H}_5$ (-) <i>cis</i> and <i>trans</i>	154 154

TABLE XXXV. SULFOXIMINES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>20</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO(C <sub>6</sub> H <sub>5</sub> )=NSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i>	NaOH, dioxane-D <sub>2</sub> O, 10:1	—	C <sub>6</sub> H <sub>5</sub> CD <sub>2</sub> SO(C <sub>6</sub> H <sub>5</sub> )=NSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> (—)	52

TABLE XXXVI. TELLURIDES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>9</sub>	HC≡CCH <sub>2</sub> TeC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> TeMgBr	—	CH <sub>2</sub> =C=CHTeC <sub>6</sub> H <sub>5</sub> (27)	61, 538



TABLE XXXVII. THIOCARBAMATES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>7</sub>	CH <sub>3</sub> CH=CHCH <sub>2</sub> SCON(CH <sub>3</sub> ) <sub>2</sub> ( <i>E</i> )	LDA, THF, -78°	CH <sub>3</sub> SSCH <sub>3</sub>	CH <sub>3</sub> CH=CHCH(SCH <sub>3</sub> )SCON(CH <sub>3</sub> ) <sub>2</sub> (-)	258b
C <sub>8</sub>	CH <sub>3</sub> CH=CHCH(SCH <sub>3</sub> )SCON(CH <sub>3</sub> ) <sub>2</sub> ( <i>E</i> )	LDA, THF, -78°	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	CH <sub>3</sub> CH=CHC(SCH <sub>3</sub> )(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )SCON(CH <sub>3</sub> ) <sub>2</sub> (-)	258b
C <sub>10</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=CHCH <sub>2</sub> SCON(CH <sub>3</sub> ) <sub>2</sub> ( <i>E</i> )	LDA, THF, -78°	CH <sub>3</sub> SSCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=CHCH(SCH <sub>3</sub> )SCON(CH <sub>3</sub> ) <sub>2</sub> (-)	258a
	<i>n</i> -C <sub>3</sub> H <sub>7</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> SCON(CH <sub>3</sub> ) <sub>2</sub> ( <i>E</i> ) and ( <i>Z</i> )	LDA (2 eq), THF, -78°	CH <sub>3</sub> SSCH <sub>3</sub> (2 eq)	<i>n</i> -C <sub>3</sub> H <sub>7</sub> (CH <sub>3</sub> )=CHC(SCH <sub>3</sub> ) <sub>2</sub> SCON(CH <sub>3</sub> ) <sub>2</sub> (-)	258b
C <sub>11</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub> CH=CHCH <sub>2</sub> SCON(CH <sub>3</sub> ) <sub>2</sub> ( <i>E</i> )	LDA, THF, -78°	CH <sub>3</sub> SSCH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub> CH=CHCH(SCH <sub>3</sub> )SCON(CH <sub>3</sub> ) <sub>2</sub> (-)	258a, 258b
		LDA (2 eq), THF, -78°	CH <sub>3</sub> SSCH <sub>3</sub> (2 eq)	<i>n</i> -C <sub>5</sub> H <sub>11</sub> CH=CHC(SCH <sub>3</sub> ) <sub>2</sub> SCON(CH <sub>3</sub> ) <sub>2</sub> (-)	258b
C <sub>12</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> SCON(CH <sub>3</sub> ) <sub>2</sub> ( <i>E</i> )	LDA, THF, -78°	CH <sub>3</sub> SSCH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub> CH=C(CH <sub>3</sub> )CH(SCH <sub>3</sub> )SCON(CH <sub>3</sub> ) <sub>2</sub> (-)	258a
	<i>n</i> -C <sub>6</sub> H <sub>13</sub> CH=CHCH <sub>2</sub> SCON(CH <sub>3</sub> ) <sub>2</sub> ( <i>E</i> )	LDA, THF, -78°	CH <sub>3</sub> SSCH <sub>3</sub>	<i>n</i> -C <sub>6</sub> H <sub>13</sub> CH=CHCH(SCH <sub>3</sub> )SCON(CH <sub>3</sub> ) <sub>2</sub> (-)	258b
		LDA (2 eq), THF, -78°	CH <sub>3</sub> SSCH <sub>3</sub> (2 eq)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> CH=CHC(SCH <sub>3</sub> ) <sub>2</sub> SCON(CH <sub>3</sub> ) <sub>2</sub> (-)	258b
	<i>n</i> -C <sub>5</sub> H <sub>11</sub> CH=CHCH(SCH <sub>3</sub> )SCON(CH <sub>3</sub> ) <sub>2</sub> ( <i>E</i> )	LDA, THF, -78°	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	<i>n</i> -C <sub>5</sub> H <sub>11</sub> CH=CHC(SCH <sub>3</sub> )(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )SCON(CH <sub>3</sub> ) <sub>2</sub> ( <i>E</i> )	258b

TABLE XXXVII. THIOCARBAMATES (Continued)

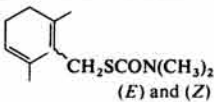
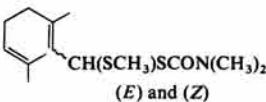
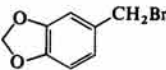
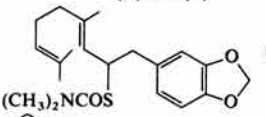
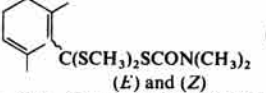
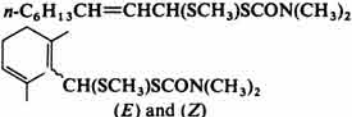
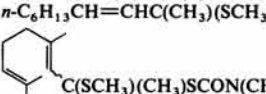
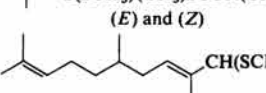
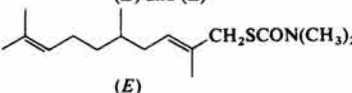
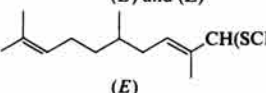
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>13</sub>		LDA, THF, -78°	CH <sub>3</sub> SSCH <sub>3</sub>	 (-)	258a, 258b
				 (-)	258a
		LDA (2 eq), THF, -78°	CH <sub>3</sub> SSCH <sub>3</sub> (2 eq)	 (-)	258b
C <sub>14</sub>		LDA, THF, -78°	CH <sub>3</sub> I	 (-)	258b
		LDA, THF, -78°	CH <sub>3</sub> I	 (-)	258b
C <sub>16</sub>		LDA, THF, -78°	CH <sub>3</sub> SSCH <sub>3</sub>	 (-)	258a

TABLE XXXVIII. THIOETHERS











No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>3</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>n</i> -C <sub>5</sub> H <sub>11</sub> , -30°, 10 min, or <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, ether, or THF	H <sub>2</sub> O	CH <sub>2</sub> =CHCH <sub>2</sub> SC <sub>4</sub> H <sub>9-n</sub>	132
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -60°, then room temperature, 1 hr	D <sub>2</sub> O	CH <sub>3</sub> CH=CHSC <sub>4</sub> H <sub>9-n</sub> <i>cis</i> and <i>trans</i> (-) CH <sub>2</sub> =CHCHDSC <sub>4</sub> H <sub>9-n</sub>	132
		CH <sub>2</sub> =CHCH(Li)SC <sub>3</sub> H <sub>7-i</sub> , TMEDA, -20°, 10 min	H <sub>2</sub> O	CH <sub>2</sub> =CHCH <sub>2</sub> SCH(SC <sub>3</sub> H <sub>7-i</sub> )CH=CH <sub>2</sub> or isomers (-)	132
		(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CLi, TMEDA, THF, -20°, 30 min		(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CCH=CHCH <sub>2</sub> SH (38)	132
C <sub>4</sub>	CH <sub>3</sub> C≡CSCH <sub>3</sub>	NaNH <sub>2</sub> , NH <sub>3</sub> (liq) LiNH <sub>2</sub> , NH <sub>3</sub> (liq)	C <sub>2</sub> H <sub>5</sub> Br CH <sub>2</sub> CH <sub>2</sub> 	HC≡CCH <sub>2</sub> CH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub> (17) CH <sub>2</sub> =C=C(SCH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> OH (88)	234 316
		LiNH <sub>2</sub> , NH <sub>3</sub> (liq), 3 min	CH <sub>3</sub> COCH <sub>3</sub>	CH <sub>2</sub> =C=C(SCH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> OH (61) CH <sub>2</sub> =C=C(SCH <sub>3</sub> )C(OH)(CH <sub>3</sub> ) <sub>2</sub> (62-66)	316 276
C <sub>5</sub>	 CH <sub>2</sub> =CHSCH <sub>2</sub> C≡CH	KNH <sub>2</sub> , NH <sub>3</sub> (liq), -60°, 10 min	CH <sub>3</sub> I	CH <sub>2</sub> =CHCH=CHSCH <sub>3</sub> (-)	193
		NaNH <sub>2</sub> (1 eq), NH <sub>3</sub> (liq)	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	CH <sub>2</sub> =CHSC(C <sub>4</sub> H <sub>9-n</sub> )=C=CH <sub>2</sub> (-)	351
C <sub>5</sub>	 	KNH <sub>2</sub> , NH <sub>3</sub> (liq)		A,  + B, 	
		LDA, THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 4:1, -60°	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Br <i>t</i> -C <sub>4</sub> H <sub>9</sub> Br		A: 85, B: 15, R =  (82) A: 100, B: 0, R = C <sub>4</sub> H <sub>9-t</sub> (54) A: 100, B: 0, R = C <sub>4</sub> H <sub>9-t</sub> (31)

TABLE XXXVIII. THIOETHERS (Continued)

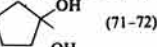
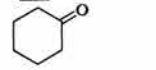
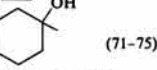
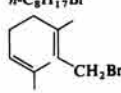
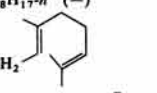

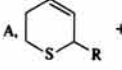
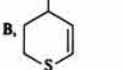


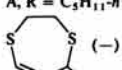
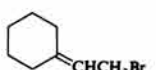
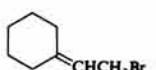
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
276	C <sub>3</sub> (Contd.) C <sub>2</sub> H <sub>5</sub> C≡CSCH <sub>3</sub> CH <sub>3</sub> C≡CSC <sub>2</sub> H <sub>5</sub>	NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	C <sub>6</sub> H <sub>5</sub> Br	HC≡CCH(CH <sub>3</sub> )CH <sub>2</sub> SC <sub>6</sub> H <sub>5</sub> (29)	234	
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 1 min	H <sub>2</sub> O	CH <sub>2</sub> =C=CHSC <sub>2</sub> H <sub>5</sub> (70-75)		133
	NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	C <sub>6</sub> H <sub>5</sub> Br	HC≡CCH <sub>2</sub> CH(CH <sub>3</sub> )SC <sub>6</sub> H <sub>5</sub> (18)	234		
	LiNH <sub>2</sub> , NH <sub>3</sub> (liq), 3 min	CH <sub>3</sub> COCH <sub>3</sub>	CH <sub>2</sub> =C=C(SC <sub>2</sub> H <sub>5</sub> )R		276	
				A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (72-75)	276	
				A, R = C(OH)(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub> (72-78)	276	
			C <sub>2</sub> H <sub>5</sub> COCH <sub>3</sub>	A, R =  (71-72)	276	
				A, R =  (71-75)	276	
	HC≡CCH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	KOH (2-4 eq), THF, 20°, 210 min	-	HC≡CCH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub> (50)	536	
				CH <sub>2</sub> =C=CHSC <sub>2</sub> H <sub>5</sub> (-)		
				CH <sub>3</sub> C≡CSC <sub>2</sub> H <sub>5</sub> (-)	61, 536	
				CH <sub>3</sub> C≡CSC <sub>2</sub> H <sub>5</sub> (66)	61, 536	
		KOH (pellets, 2 eq), THF, 55°, 30 min	-	CH <sub>2</sub> =C=CHSC <sub>2</sub> H <sub>5</sub> (43)	61, 538	
		C <sub>2</sub> H <sub>5</sub> ONa (0.1 eq), C <sub>2</sub> H <sub>5</sub> OH, 70°, 12 min	-	CH <sub>2</sub> =C=C(C <sub>2</sub> H <sub>5</sub> )SC <sub>2</sub> H <sub>5</sub> (70-75)	133	
	NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	C <sub>2</sub> H <sub>5</sub> Br	CH <sub>2</sub> =C=C(SC <sub>2</sub> H <sub>5</sub> )C <sub>2</sub> H <sub>5</sub> -i (70-75)	133		
CH <sub>2</sub> =C=CHSC <sub>2</sub> H <sub>5</sub>	sec-C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	i-C <sub>2</sub> H <sub>5</sub> Br	CH <sub>2</sub> =CHCHRSCH=CH <sub>2</sub>	129		
CH <sub>2</sub> =CHCH <sub>2</sub> SCH=CH <sub>2</sub>		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (85)	129		
		n-C <sub>8</sub> H <sub>17</sub> Br	A, R = C <sub>8</sub> H <sub>17</sub> -n (-)	129		
			A, R = 	129		
277		n-C <sub>4</sub> H <sub>9</sub> Li (1.2 eq), TMEDA, THF, -49°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl, -49°, 2 hr	A,  + B, 	A (68), B (24), R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	278
		sec-C <sub>4</sub> H <sub>9</sub> Li (1.2 to 2 eq), THF, -78°	n-C <sub>4</sub> H <sub>9</sub> Cl, -78°, 2 hr	A (69), B (1), R = C <sub>4</sub> H <sub>9</sub> -n	278	
			n-C <sub>4</sub> H <sub>9</sub> Br, -78°, 90 min	A (73), B (7), R = C <sub>4</sub> H <sub>9</sub> -n	278	
			n-C <sub>4</sub> H <sub>9</sub> I, -78°, 45 min	A (70), B (30), R = C <sub>4</sub> H <sub>9</sub> -n	278	
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl, -78°, 2 hr	A (62), B (25.7), R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	278	
			ClCH <sub>2</sub> CH <sub>2</sub> Cl, -78°, 1 hr	A (95), B (trace), R = CH <sub>2</sub> CH <sub>2</sub> Cl	278	
				A (36), B (17), R = CH <sub>2</sub> CH(OH)CH <sub>3</sub>	278	
			CH <sub>3</sub> CHCH <sub>2</sub> , -78°, 3 hr			
			n-C <sub>6</sub> H <sub>13</sub> CHO, -78°	A (0), B (94), R = CH(OH)C <sub>6</sub> H <sub>13</sub> -n	278	
			n-C <sub>6</sub> H <sub>13</sub> COCH <sub>3</sub> , -78°, 2.25 hr	A (0), B (73), R = C(OH)(CH <sub>3</sub> )C <sub>6</sub> H <sub>13</sub> -n	278	
			CH <sub>3</sub> I	CH <sub>3</sub> SCR=C=CHOCH <sub>3</sub>		
				A, R = CH <sub>3</sub> (73)	136	
				A, R = C <sub>2</sub> H <sub>5</sub> (93)	136	
			C <sub>2</sub> H <sub>5</sub> Br	A, R = CH <sub>2</sub> CH <sub>2</sub> O THP (93)	136	
		ClCH <sub>2</sub> CH <sub>2</sub> O THP	A, R = CH <sub>2</sub> CH <sub>2</sub> O THP (82)	136		
		BrCH <sub>2</sub> CH <sub>2</sub> O THP	A, R = C <sub>2</sub> H <sub>5</sub> -i (54)	136		
		i-C <sub>2</sub> H <sub>5</sub> Br	A, R = C <sub>3</sub> H <sub>7</sub> -i (86)	136		
		i-C <sub>2</sub> H <sub>5</sub> Br, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (1 eq)	A, R = C <sub>2</sub> H <sub>11</sub> -n	136		
		n-C <sub>3</sub> H <sub>11</sub> I				
		n-C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 2 hr	CH <sub>3</sub> I	 (-)	513	
	CH <sub>3</sub> CH=CHSC <sub>2</sub> H <sub>5</sub>	KNH <sub>2</sub> , NH <sub>3</sub> (liq)	n-C <sub>4</sub> H <sub>9</sub> Br	CH <sub>2</sub> =CHCH(C <sub>4</sub> H <sub>9</sub> -n)SC <sub>2</sub> H <sub>5</sub>	352	
				+ n-C <sub>3</sub> H <sub>11</sub> CH=CHSC <sub>2</sub> H <sub>5</sub>		
				cis and trans (-)		
				CH <sub>3</sub> CH=CHSC <sub>2</sub> H <sub>5</sub>	352	
				cis and trans (90-93)		
	CH <sub>2</sub> =CHCH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	i-C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> , 40-50°, 10 min	H <sub>2</sub> O	CH <sub>2</sub> =CHCH(C <sub>4</sub> H <sub>9</sub> -n)SC <sub>2</sub> H <sub>5</sub>	352	
		KNH <sub>2</sub> , NH <sub>3</sub> (liq)	n-C <sub>4</sub> H <sub>9</sub> Br	+ n-C <sub>3</sub> H <sub>11</sub> CH=CHSC <sub>2</sub> H <sub>5</sub>		
				cis and trans (-)		
				CH <sub>3</sub> SCH <sub>2</sub> CH=CHOCH <sub>3</sub>	428	
				cis (32), trans (65)		
				+ CH <sub>3</sub> SCH=CHCH <sub>2</sub> OCH <sub>3</sub>		
				cis (1), trans (2)		
				CH <sub>3</sub> SCH=CHCHRSCH <sub>3</sub>		
	CH <sub>3</sub> SCH=CHCH <sub>2</sub> OCH <sub>3</sub> cis: 3, trans: 7	i-C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub>	-	A, R =  (92)	282	
	CH <sub>3</sub> SCH=CHCH <sub>2</sub> SCH <sub>3</sub>	sec-C <sub>4</sub> H <sub>9</sub> Li, ether, -78°, then -26°, 30 min, CuI (1.2 eq), -78°, 15 min	 (0.5 eq)			

TABLE XXXVIII. THIOETHERS (Continued)

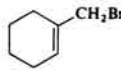
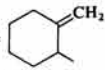
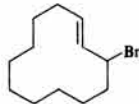
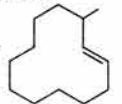

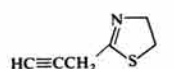
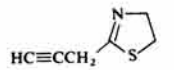
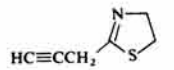
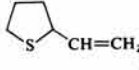

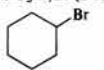
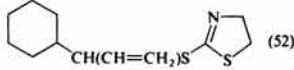

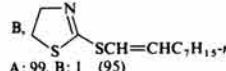
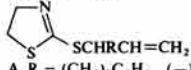
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>5</sub> (Contd.)	CH <sub>3</sub> SCH=CHCH <sub>2</sub> SCH <sub>3</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -78°, then -26°, 30 min, CuI (1.2 eq), -78°, 15 min	 (0.5 eq)	A, R =  (-)	282	
			(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Br (0.5 eq)	not isolated A, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (-) not isolated	283	
			 (0.5 eq)	A, R =  (-) not isolated	282	
278 C <sub>6</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, -60°	CH <sub>3</sub> I	HC≡CCHRS A, R = CH <sub>3</sub> (60) A, R = CH <sub>2</sub> C≡CH (50) A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (35) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (65) A, R = CH <sub>2</sub> C≡CC <sub>6</sub> H <sub>5</sub> (60) A, R = CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (50)	311, 430 311, 430 430 311, 430 311, 430 311	
			HC≡CCH <sub>2</sub> Br CH <sub>2</sub> =CHCH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> C≡CCH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CHO	HC≡CCHRS A, R = CH <sub>3</sub> (60) A, R = CH <sub>2</sub> C≡CH (50) A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (35) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (65) A, R = CH <sub>2</sub> C≡CC <sub>6</sub> H <sub>5</sub> (60) A, R = CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (50)	311, 430 311, 430 430 311, 430 311, 430 311	
			C <sub>6</sub> H <sub>5</sub> CHCHC≡CH cis: 1, trans: 1 + C <sub>6</sub> H <sub>5</sub> CH=CHC≡CH cis: 1, trans: 1 + C <sub>6</sub> H <sub>5</sub> CH=CHC≡CCH(OH)C <sub>6</sub> H <sub>5</sub> (20) CH <sub>2</sub> =CHCH=C=CHSCH <sub>3</sub> (45)	247, 430		
						
	CH <sub>3</sub> CH=CHC≡CSCH <sub>3</sub> cis: 70, trans: 30		NaNH <sub>2</sub> (1.4 eq), NH <sub>3</sub> (liq), 2 min C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 30 min	H <sub>2</sub> O H <sub>2</sub> O	No reaction	590 590
	CH <sub>2</sub> =CHC≡CCH <sub>2</sub> SCH <sub>3</sub>		NaNH <sub>2</sub> (1.4 eq), NH <sub>3</sub> (liq), 3 min	H <sub>2</sub> O	CH <sub>2</sub> =CHCH=C=CHSCH <sub>3</sub> (100)	590
			C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 1 min	H <sub>2</sub> O	CH <sub>2</sub> CH=CHC≡CSCH <sub>3</sub> cis: 60, trans: 40 (100)	590
	CH <sub>2</sub> =C=C=CHSC <sub>2</sub> H <sub>5</sub> CH <sub>2</sub> =CHSCH <sub>2</sub> C≡CCH <sub>3</sub> CH <sub>2</sub> CH=CHSCH <sub>2</sub> C≡CH CH <sub>2</sub> =C(CH <sub>3</sub> )SCH <sub>2</sub> C≡CH		C <sub>2</sub> H <sub>5</sub> ONa, NH <sub>3</sub> (liq) NaNH <sub>2</sub> (1 eq), NH <sub>3</sub> (liq) NaNH <sub>2</sub> (1 eq), NH <sub>3</sub> (liq) NaNH <sub>2</sub> (1 eq), NH <sub>3</sub> (liq)	H <sub>2</sub> O <i>n</i> -C <sub>4</sub> H <sub>9</sub> Br <i>n</i> -C <sub>4</sub> H <sub>9</sub> Br <i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	CH <sub>2</sub> =CHC≡CSC <sub>2</sub> H <sub>5</sub> (84) CH <sub>2</sub> =CHSC(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )=C=CHCH <sub>3</sub> (-) CH <sub>2</sub> CH=CHSC(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )=C=CH <sub>2</sub> (-) CH <sub>2</sub> =C(CH <sub>3</sub> )SC(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )=C=CH <sub>2</sub> (-)	170 351 351 351
	CH <sub>2</sub> =CHCH <sub>2</sub> S(CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> Br		LDA, THF, -70°	-	 (85)	227
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -60°	CH <sub>3</sub> I	CH <sub>2</sub> =CHCHRS A, R = CH <sub>3</sub> (68) A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (60) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (78)	311, 429 311, 429 311, 429
	CH <sub>2</sub> =CHCH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br					
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, -60°	C <sub>2</sub> H <sub>5</sub> Br (2 eq)	CH <sub>2</sub> =CHCR <sub>2</sub> S A, R = C <sub>2</sub> H <sub>5</sub> (40) A, R = C <sub>3</sub> H <sub>7</sub> - <i>n</i> (35)	311 311		
		<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br (2 eq)				
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 10:1, -60°		 (52)	46		
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 5%, -65°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	A,  SCH(C <sub>6</sub> H <sub>13</sub> - <i>n</i> )CH=CH <sub>2</sub> + B,  SCH=CHC, H <sub>13</sub> - <i>n</i> A: 99, B: 1 (95)	8		
		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> Br	 SCHRCH=CH <sub>2</sub> A, R = (CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (-) A, R = C <sub>10</sub> H <sub>21</sub> - <i>n</i> (70) (CH <sub>3</sub> CH=CH) <sub>2</sub> S (58) cis: 60, trans: 40	46 46 540		
[CH <sub>2</sub> =CHCH <sub>2</sub> ] <sub>2</sub> S	<i>t</i> -C <sub>4</sub> H <sub>9</sub> ONa (0.51 eq), room temperature, 22 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -15°, 1 hr	<i>n</i> -C <sub>10</sub> H <sub>21</sub> Br -	CH <sub>2</sub> =CHCHSRCH <sub>2</sub> CH=CH <sub>2</sub> A, R = CH <sub>3</sub> (98) A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (98) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (94)	216 216 216		
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -78°, 1 hr	CH <sub>2</sub> =CHCH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br				

TABLE XXXVIII. THIOETHERS (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>6</sub> (Contd.)	[CH <sub>2</sub> =CHCH <sub>2</sub> ] <sub>2</sub> S	C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH, reflux, 12 hr	—	(CH <sub>2</sub> CH=CH) <sub>2</sub> S (—) + CH <sub>2</sub> =CHCH <sub>2</sub> SCH=CHCH <sub>3</sub> (—) + CH <sub>2</sub> =CHCH <sub>2</sub> CH(SH)CH=CH <sub>2</sub> (—) CH <sub>3</sub> CH=C=C(C <sub>2</sub> H <sub>5</sub> )SC <sub>2</sub> H <sub>5</sub> (70-75) CH <sub>3</sub> CH=C=CHSC <sub>2</sub> H <sub>5</sub> (65-70) CH <sub>3</sub> CH=C=C(C <sub>3</sub> H <sub>7-n</sub> )SC <sub>2</sub> H <sub>5</sub> (80)	217	
	CH <sub>3</sub> CH=C=CHSC <sub>2</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub> C≡CSC <sub>2</sub> H <sub>5</sub>	NaNH <sub>2</sub> , NH <sub>3</sub> (liq) NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 5 min NaNH <sub>2</sub> (1 eq), NH <sub>3</sub> (liq), 10 min	C <sub>2</sub> H <sub>5</sub> Br H <sub>2</sub> O <i>n</i> -C <sub>3</sub> H <sub>7</sub> Br <i>i</i> -C <sub>3</sub> H <sub>7</sub> Br <i>n</i> -C <sub>4</sub> H <sub>9</sub> Br <i>n</i> -C <sub>5</sub> H <sub>11</sub> Br <i>n</i> -C <sub>6</sub> H <sub>13</sub> Br	CH <sub>3</sub> CH=C=C(C <sub>3</sub> H <sub>7-i</sub> )SC <sub>2</sub> H <sub>5</sub> (80) CH <sub>3</sub> CH=C=C(C <sub>4</sub> H <sub>9-n</sub> )SC <sub>2</sub> H <sub>5</sub> (80) CH <sub>3</sub> CH=C=C(C <sub>5</sub> H <sub>11-n</sub> )SC <sub>2</sub> H <sub>5</sub> (80) CH <sub>3</sub> CH=C=C(C <sub>6</sub> H <sub>13-n</sub> )SC <sub>2</sub> H <sub>5</sub> (80)	133 133 181 181 181 181	
280		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), THF, TMEDA (1 eq), -5°	D <sub>2</sub> O	(-) +  (traces)	130	
				(-)	130, 382	
				(-) + (8)	130	
			CICH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OLi, ( <i>E</i> ) -20°	R	A, R = CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OH (—) A, R = CH <sub>2</sub> CH(OH)CH <sub>3</sub> (75)	130 481
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA, -50°, 2 hr	CH <sub>3</sub> CHCH <sub>2</sub> 	A, R = CH <sub>2</sub> CH(OH)C <sub>2</sub> H <sub>5</sub> (—)	481	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA, -50°, 2 hr	C <sub>2</sub> H <sub>5</sub> CHCH <sub>2</sub> 	A, R =  (—) A, R = CH <sub>2</sub> CH(OH)C <sub>6</sub> H <sub>5</sub> (—)	142, 481 481	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -20°		A, R =	479	
	CH <sub>3</sub> SCH <sub>2</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> <i>trans</i>	LDA, THF, -78°, 30 min	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, CH <sub>3</sub> I	CH <sub>3</sub> SCH=CHCHRCO <sub>2</sub> CH <sub>3</sub> <i>cis</i> and <i>trans</i> A, R = CH <sub>3</sub> (92) A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (63) A, R = CH <sub>2</sub> C≡CH (65) A, CH <sub>2</sub> =C=C=CHSCH <sub>3</sub> + B, CH <sub>2</sub> =CHC≡CSCH <sub>3</sub> A: 90-85, B: 10-15 (63-65)	470 470 470	
	CH <sub>3</sub> SCH <sub>2</sub> C≡CCH <sub>2</sub> SCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -50°, 35 min	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, CH <sub>2</sub> =CHCH <sub>2</sub> Br [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, HC≡CCH <sub>2</sub> Br H <sub>2</sub> O	RCH <sub>2</sub> CH=CHSC <sub>3</sub> H <sub>7-i</sub> A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (88)	170, 277 282, 283	
	CH <sub>2</sub> =CHCH <sub>2</sub> SC <sub>3</sub> H <sub>7-i</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -78°, then -26°, 30 min, CuI (1.2 eq) -78°, 15 min	CH <sub>2</sub> =CHCH <sub>2</sub> Br (0.5 eq)	A, R =  (92)	282, 283	
			(0.5 eq) CH <sub>2</sub> Br	A, R =  (87)	282, 283	

TABLE XXXVIII. THIOETHERS (Continued)











No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>6</sub> (Contd.)	CH <sub>2</sub> =CHCH <sub>2</sub> SC <sub>3</sub> H <sub>7-i</sub>	sec-C <sub>4</sub> H <sub>9</sub> Li, ether, -78°, then -26°, 30 min, CuI (1.2 eq), -78°, 15 min	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (0.5 eq) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCl CH <sub>3</sub> COCH <sub>3</sub> (excess)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (78) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (70) A, CH <sub>2</sub> =CHCH[C(OH)(CH <sub>3</sub> ) <sub>2</sub> ]SC <sub>3</sub> H <sub>7-i</sub> + B, (CH <sub>3</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> CH=CHSC <sub>3</sub> H <sub>7-i</sub> A: 20, B: 1 (89) A, <i>i</i> -C <sub>3</sub> H <sub>7</sub> SCH(R)CH=CH <sub>2</sub> + B, <i>i</i> -C <sub>3</sub> H <sub>7</sub> SCH=CHCH <sub>2</sub> R A: 28, B: 72, R = C <sub>6</sub> H <sub>5</sub> CH(OH) (-) A: 98, B: 2, R = C <sub>6</sub> H <sub>5</sub> CH(OH) (82)	282 282
		sec-C <sub>4</sub> H <sub>9</sub> Li, ether, -78°C, then -30°, 30 min	C <sub>6</sub> H <sub>5</sub> CHO  (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> B, -78°, then C <sub>6</sub> H <sub>5</sub> CHO, -0°, 1 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> -9-BBN, -78°, then C <sub>6</sub> H <sub>5</sub> CHO <i>n</i> -C <sub>3</sub> H <sub>7</sub> CHO, (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> B, -78°, then <i>n</i> -C <sub>3</sub> H <sub>7</sub> CHO, 0°, 1 hr (CH <sub>3</sub> ) <sub>2</sub> CHCHO (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> B, -78°, then (CH <sub>3</sub> ) <sub>2</sub> CHCHO, 0°, 1 hr  (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> B, -78°, then  0°, 1 hr CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COCH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> B, -78°, then CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COCH <sub>3</sub> , 0°, 1 hr <i>n</i> -C <sub>4</sub> H <sub>9</sub> -9-BBN, -78°, 10 min, then CH <sub>2</sub> =CHCH <sub>2</sub> Br, room temperature overnight	A: 99, B: 1, R = C <sub>6</sub> H <sub>5</sub> CH(OH) (70) A: 43, B: 57, R = <i>n</i> -C <sub>3</sub> H <sub>7</sub> CH(OH) (-) A: 94, B: 6, R = <i>n</i> -C <sub>3</sub> H <sub>7</sub> CH(OH) (76) A: 44, B: 56, R = (CH <sub>3</sub> ) <sub>2</sub> CHCH(OH) (-) A: 94, B: 6, R = (CH <sub>3</sub> ) <sub>2</sub> CHCH(OH) (75) A: 42, B: 58, R =  (-) A: 72, B: 28, R =  (80) A: 32, B: 68, R = CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> C(OH)CH <sub>3</sub> (-) A: 47, B: 53, R = CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> C(OH)CH <sub>3</sub> (70) A: 89, B: 1, R = CH <sub>2</sub> CH=CH <sub>2</sub> (58)	282, 283 284a 284a 284a 284a 284a 284a 284a 284b
			CH <sub>3</sub> CH=CHCH <sub>2</sub> Br (CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Cl	A: 100, B: 0, R = CH <sub>2</sub> CH=CHCH <sub>3</sub> (77) A, <i>i</i> -C <sub>3</sub> H <sub>7</sub> SCHCH=CH <sub>2</sub> + C(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub> + B, <i>i</i> -C <sub>3</sub> H <sub>7</sub> SCHCH=CH <sub>2</sub> + CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> A: 93, B: 7 (68)	284b 284b
	CH <sub>3</sub> SCH <sub>2</sub> CH(OCH <sub>3</sub> )CH <sub>2</sub> SCH <sub>3</sub>	LDA (2 eq), THF, -75°, then 0°, 8 hr		 CH(SCH <sub>3</sub> )CH=CHSCH <sub>3</sub> <i>cis</i> and <i>trans</i> (99)	314
		LDA (2 eq), THF, -75°, then -15°, 21-70 hr; or 0°, 8 hr; or 25°, 100 min	 -78°, 4 hr	A,  + B,  CH <sub>3</sub> SCH=CHCHSCH <sub>3</sub> A: 3, B: 4 (-) CH <sub>3</sub> SCH(R)CH=CHSCH <sub>3</sub> A, R = C <sub>2</sub> H <sub>5</sub> - <i>n</i> (90) <i>cis</i> : 20, <i>trans</i> : 80 A, R = CH <sub>2</sub> CH(OH)CH <sub>3</sub> (97) <i>cis</i> and <i>trans</i>	329
			<i>n</i> -C <sub>3</sub> H <sub>11</sub> Br, -75°, 2 hr CH <sub>3</sub> CHCH <sub>2</sub> , -75°, 12 hr  C <sub>2</sub> H <sub>5</sub> CHO, -75°, 5 min, then 20°, 30 min CH <sub>3</sub> COCH <sub>3</sub> , -75°, 5 min, then 18°, 5 min C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> , -75°, 5 min, then 18°, 5 min	A, R = CH(OH)C <sub>2</sub> H <sub>5</sub> (85-89) <i>cis</i> and <i>trans</i> A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (97) <i>cis</i> and <i>trans</i> A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (95) <i>cis</i> : 4, <i>trans</i> : 5	314 314 314

TABLE XXXVIII. THIOETHERS (Continued)









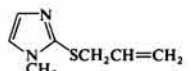
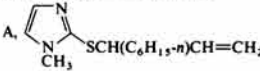
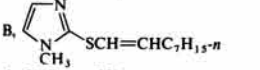




No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>6</sub> (Contd.)	<chem>CH3SCH2CH(OCH3)CH2SCH3</chem>	LDA (2 eq), THF, -75°, then -15°, 21-70 hr, or 0°, 8 hr; or 25°, 100 min	 -75°, 5 hr	A, R =  (96) cis and trans	314
		LDA, THF	 then (CH <sub>3</sub> CO) <sub>2</sub> O	A, R =  (-)	360
			 then (CH <sub>3</sub> CO) <sub>2</sub> O	A, R =  (-)	360
C <sub>7</sub>	<chem>CH3C#CCCH2S</chem> 	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, -60°, 20 min	CH <sub>3</sub> I	<chem>CH3C#CCCHRS</chem>  A, R = CH <sub>3</sub> (55) A, R = CH <sub>2</sub> C≡CH (45) A, R = CH <sub>2</sub> C≡CCH <sub>3</sub> (42) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (48) A, R = CH <sub>2</sub> C≡CC <sub>6</sub> H <sub>5</sub> (48)	430 430 430 311, 430 311, 430
			HC≡CCH <sub>2</sub> Br CH <sub>3</sub> C≡CCH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> C≡CCH <sub>2</sub> Br		
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	A,  SCH(C <sub>6</sub> H <sub>13</sub> , <i>n</i> )CH=CH <sub>2</sub> + B,  SCH=CHC <sub>7</sub> H <sub>15</sub> , <i>n</i> A: 99, B: 1 (92) A: >99, B: <1 (92)	8 8
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 5%, -65°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°		
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>n</i> -C <sub>5</sub> H <sub>12</sub> , -10°, 4 hr	H <sub>2</sub> O	 CH <sub>2</sub> SC <sub>4</sub> H <sub>9</sub> , <i>t</i> (80)	132
	<chem>CH3CH=CHC#CCCH2SCH3</chem> cis: 60, trans: 40	NaNH <sub>2</sub> (1.4 eq), NH <sub>3</sub> (liq), 3 min	H <sub>2</sub> O	A, CH <sub>3</sub> CH=CHC≡CCH <sub>2</sub> SCH <sub>3</sub> + B, CH <sub>3</sub> CH=CHCH=C=CHSCH <sub>3</sub> A: 50, B: 50 (85) A cis: 40, B: 60 (-)	590 590
		C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 45 min	H <sub>2</sub> O	A trans: 10, B: 90 (-) A cis: 75, B: 25 (-)	590 590
	<chem>CH3CH=CHCH=C=CHSCH3</chem> cis: 1, trans: 99	C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 45 min	H <sub>2</sub> O	A, CH <sub>3</sub> CH=CHC≡CCH <sub>2</sub> SCH <sub>3</sub> cis + B, CH <sub>3</sub> CH=CHCH=C=CHSCH <sub>3</sub> A: 30, B: 70 (-)	590
		C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 45 min	H <sub>2</sub> O	A, CH <sub>3</sub> CH=CHC≡CCH <sub>2</sub> SCH <sub>3</sub> cis + B, CH <sub>3</sub> CH=CHCH=C=CHSCH <sub>3</sub> + C, C <sub>2</sub> H <sub>5</sub> CH=CHC≡CSCH <sub>3</sub> A cis: 25, B: 15, C: 15 (cis: 45, trans: 55) (-) C cis: 100 (-) A cis: 21, B: 9, C trans: 70 (-)	590 590 590
	<chem>C2H5CH=CHC#CCSCH3</chem> cis: 45, trans: 55	C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 60 min	H <sub>2</sub> O	A, CH <sub>3</sub> CH=CHC≡CCH <sub>2</sub> SCH <sub>3</sub> + B, CH <sub>3</sub> CH=CHCH=C=CHSCH <sub>3</sub> + C, C <sub>2</sub> H <sub>5</sub> CH=CHC≡CSCH <sub>3</sub> A cis: 25, B: 15, C: 15 (cis: 45, trans: 55) (-) C cis: 100 (-) A cis: 21, B: 9, C trans: 70 (-)	590 590 590
		C <sub>2</sub> H <sub>5</sub> ONa (1.4 eq), NH <sub>3</sub> (liq), 5 min	H <sub>2</sub> O	A, CH <sub>3</sub> CH=CHCH=C=CHSCH <sub>3</sub> + B, C <sub>2</sub> H <sub>5</sub> CH=CHC≡CSCH <sub>3</sub> A: 95, B: 5 (20) A: 37, B: 63 (28) A: 55, B: 45 (30)	590 590 590
	<chem>C2H5CH=C=C=CHSCH3</chem> cis and trans	C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 5 min	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> CH=CHC≡CSCH <sub>3</sub> cis and trans (-)	590
		NaNH <sub>2</sub> (1.4 eq), NH <sub>3</sub> (liq), 5 min	H <sub>2</sub> O	CH <sub>2</sub> =C(CH <sub>3</sub> )CH=C=CHSCH <sub>3</sub> (80)	590
	<chem>CH2=C(CH3)C#CCCH2SCH3</chem>	C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 30 min	H <sub>2</sub> O	No reaction	590
		C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 15 min	H <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=C=CHC≡CSCH <sub>3</sub> (100)	590
	<chem>CH2=C(CH3)CH=C=CHSCH3</chem>	NaNH <sub>2</sub> (1.4 eq), NH <sub>3</sub> (liq), 3 min	H <sub>2</sub> O	CH <sub>2</sub> =C(CH <sub>3</sub> )CH=C=CHSCH <sub>3</sub> (80)	590
		C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 15 min	H <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=C=CHC≡CSCH <sub>3</sub> (100)	590
	<chem>CH2=C(CH3)CH2S</chem> 	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -60°	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br	CH <sub>2</sub> =C(CH <sub>3</sub> )CHRS  A, R = C <sub>3</sub> H <sub>7</sub> , <i>n</i> (63) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (65) A, R = C <sub>10</sub> H <sub>21</sub> , <i>n</i> (70)	311 311 311
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br		
			<i>n</i> -C <sub>10</sub> H <sub>21</sub> Br		



TABLE XXXVIII. THIOETHERS (Continued)

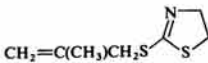
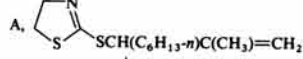
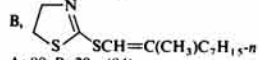
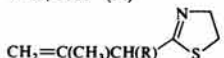
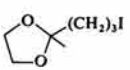
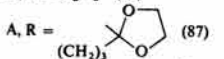
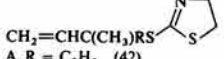
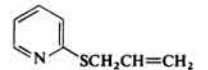
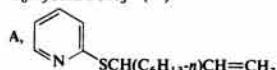
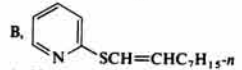

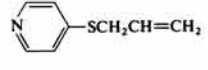
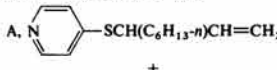
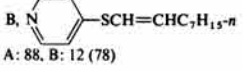
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>7</sub> (Cont'd.)		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, 5% [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -65°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	A,  SCH(C <sub>6</sub> H <sub>13</sub> - <i>n</i> )C(CH <sub>3</sub> )=CH <sub>2</sub> + B,  SCH=C(CH <sub>3</sub> )C <sub>7</sub> H <sub>15</sub> - <i>n</i> A: 80, B: 20 (94)	8
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	C <sub>2</sub> H <sub>5</sub> Br	 CH <sub>2</sub> =C(CH <sub>3</sub> )CH(R) A, R = C <sub>2</sub> H <sub>5</sub> (80)	483
				A, R =  (87)	483
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 20:1, -60°	C <sub>2</sub> H <sub>5</sub> I	 CH <sub>2</sub> =CHC(CH <sub>3</sub> )RS A, R = C <sub>2</sub> H <sub>5</sub> (42)	311
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br <i>n</i> -C <sub>10</sub> H <sub>21</sub> Br C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (40) A, R = C <sub>10</sub> H <sub>21</sub> - <i>n</i> (56)	311 311
		LDA, THF, -60°, 1 hr, then [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (1 eq), 30 min	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br <i>n</i> -C <sub>10</sub> H <sub>21</sub> Br C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> SC(CH <sub>3</sub> )=C=C(CH <sub>3</sub> )C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (-)	136
		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	CH <sub>2</sub> =CHCH <sub>2</sub> Br	CH <sub>2</sub> =C(OC <sub>2</sub> H <sub>5</sub> )CHRSCCH=CH <sub>2</sub> A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (-)	131
			C <sub>2</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> Br <i>cis</i>	A, R = CH <sub>2</sub> CH=CHC <sub>2</sub> H <sub>5</sub> (-)	131
		LDA, THF, -78°, 30 min	<i>n</i> -C <sub>5</sub> H <sub>11</sub> Br [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, CH <sub>3</sub> I	A, R = C <sub>5</sub> H <sub>11</sub> - <i>n</i> (-) CH <sub>3</sub> SCCH=CHC(CH <sub>3</sub> )RCO <sub>2</sub> CH <sub>3</sub> A, R = CH <sub>3</sub> (95)	470
		<i>n</i> -C <sub>3</sub> H <sub>7</sub> C≡CSC <sub>2</sub> H <sub>5</sub> HC≡CCH <sub>2</sub> SC <sub>4</sub> H <sub>9</sub> - <i>t</i>	NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 5 min KOH (pellets, 2 eq), THF, room temperature, 3 hr	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, CH <sub>2</sub> =CHCH <sub>2</sub> Br [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, HC≡CCH <sub>2</sub> Br H <sub>2</sub> O	A, R = CH <sub>2</sub> CH=CH <sub>2</sub> (80) A, R = CH <sub>2</sub> C≡CH (49) C <sub>2</sub> H <sub>5</sub> CH=C=CHSC <sub>2</sub> H <sub>5</sub> (65-70) CH <sub>2</sub> =C=CHSC <sub>4</sub> H <sub>9</sub> - <i>t</i> (67)
C <sub>8</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> SC <sub>4</sub> H <sub>9</sub> - <i>t</i>	C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH, reflux 1 hr	-	CH <sub>2</sub> CH=CHSC <sub>4</sub> H <sub>9</sub> - <i>t</i> (66) <i>cis</i> and <i>trans</i>	217
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> ONa (1 eq), room temperature, 11 days	-	CH <sub>3</sub> CH=CHSC <sub>4</sub> H <sub>9</sub> - <i>t</i> (48)	540
	C <sub>2</sub> H <sub>5</sub> SCH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, 0°, 1 hr	D <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> SCHDCH=C(CH <sub>3</sub> ) <sub>2</sub> (98)	44, 220
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -20°, 1 hr	CH <sub>2</sub> =CHCH <sub>2</sub> Br	A, C <sub>2</sub> H <sub>5</sub> SCHRCH=C(CH <sub>3</sub> ) <sub>2</sub> + B, C <sub>2</sub> H <sub>5</sub> SCH=CHCR(CH <sub>3</sub> ) <sub>2</sub> + C, C <sub>2</sub> H <sub>5</sub> SCH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> A: 70, B: 26.5, C: 3.5, R = CH <sub>2</sub> CH=CH <sub>2</sub> (95)	220
			(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Br	A: 80, B: 15, C: 5, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (91)	220
	<i>n</i> -C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> CH=CHSCH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> , room temperature, 30 min	-	A, <i>n</i> -C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> CH=CHSCH <sub>3</sub> <i>cis</i> : 29, <i>trans</i> : 38 + B, <i>n</i> -C <sub>3</sub> H <sub>7</sub> CH=CHCH <sub>2</sub> SCH <sub>3</sub> A: 67, B: 33 (-)	522
			-	<i>o</i> -CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> SH (-)	222
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SCH <sub>3</sub>	KNH <sub>2</sub> , NH <sub>3</sub> (liq), ether, room temperature, 1.5 hr, then reflux of ether, 16 hr	-	C <sub>6</sub> H <sub>5</sub> CHDSCH <sub>3</sub> (-)	180
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 2 hr	D <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CHDSCH <sub>3</sub> (-)	180
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	A,  SCH(C <sub>6</sub> H <sub>13</sub> - <i>n</i> )CH=CH <sub>2</sub> + B,  SCH=CHC <sub>7</sub> H <sub>15</sub> - <i>n</i> A: 99, B: 1 (90) A: >99, B: <1 (90)	8 8
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, 5% [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -65°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°			
	C <sub>6</sub> H <sub>5</sub> Li, THF, -25° to -15°	C <sub>2</sub> H <sub>5</sub> Br	 SCHRCH=CH <sub>2</sub> A, R = C <sub>2</sub> H <sub>5</sub> (95)	269	
		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> Br	A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (79-82) A, R = CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (82)	269, 300 269	
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, 5% [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 65°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	A,  SCH(C <sub>6</sub> H <sub>13</sub> - <i>n</i> )CH=CH <sub>2</sub> + B,  SCH=CHC <sub>7</sub> H <sub>15</sub> - <i>n</i> A: 88, B: 12 (78)	8	

TABLE XXXVIII. THIOETHERS (Continued)

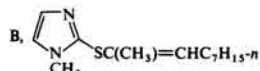
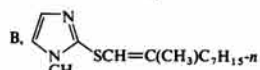
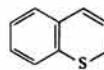
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub> (Contd.)		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -65°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	A,  + B,  A: 80, B: 20 (-)	8
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	A,  + B,  A: 92, B: 8 (86)	8
288		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	A,  + B,  A: 92, B: 8 (86)	8
	C <sub>2</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CHC≡CSCH <sub>3</sub>  cis: 30, trans: 70 cis: 97, trans: 3 cis: 4, trans: 96 CH <sub>2</sub> =C(CH <sub>3</sub> )CH=C=CHSC <sub>2</sub> H <sub>5</sub> CH <sub>3</sub> SC(C <sub>2</sub> H <sub>5</sub> )=C=CHOC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> ONa (0.3 eq), NH <sub>3</sub> (liq), 5 min  LiNH <sub>2</sub> , NH <sub>3</sub> (liq), 15 min LDA, THF, -60°, 2 hr  LDA, THF, -60°, 1 hr, then [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (1 eq), 30 min	H <sub>2</sub> O  CH <sub>3</sub> CHO CH <sub>3</sub> COCH <sub>3</sub>  C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	A, CH <sub>2</sub> =C(C <sub>2</sub> H <sub>5</sub> )CH=C=CHSCH <sub>3</sub> + B, CH <sub>3</sub> CH=C(CH <sub>3</sub> )CH=C=CHSCH <sub>3</sub> A: 80, B: 20 (67) A: 74, B: 26 (65) A: 76, B: 24 (68) CH <sub>2</sub> =C(CH <sub>3</sub> )CH=C=C(SC <sub>2</sub> H <sub>5</sub> )CH(OH)CH <sub>3</sub> (28) CH <sub>3</sub> SC(C <sub>2</sub> H <sub>5</sub> )=C=CROCC <sub>2</sub> H <sub>5</sub> A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (-) A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (-)	590 590 590 182 136 136
	C <sub>2</sub> H <sub>5</sub> SCH <sub>2</sub> C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> ONa (1 eq), NH <sub>3</sub> (liq), 48 hr	H <sub>2</sub> O	CH <sub>2</sub> =CHC≡CSC <sub>2</sub> H <sub>5</sub> (71) + C <sub>2</sub> H <sub>5</sub> SCH <sub>2</sub> C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> (20)	182
	C <sub>2</sub> H <sub>5</sub> OCH(CH <sub>3</sub> )C≡CCH <sub>2</sub> SCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -50°, 35 min	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> SCH=C=CHCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> (-) A, CH <sub>3</sub> CH=C=C=CHSCH <sub>3</sub> + B, CH <sub>3</sub> CH=CHC≡CSCH <sub>3</sub> A: 65, B: 35 (70) CH <sub>3</sub> SCR=C=C(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> A, R = CH <sub>3</sub> (99) A, R = C <sub>2</sub> H <sub>5</sub> (89) A, R = CH <sub>2</sub> C <sub>2</sub> H <sub>5</sub> - <i>i</i> (80) A, R = CH(OH)CH <sub>3</sub> (-) A, R = CH(OH)C <sub>2</sub> H <sub>5</sub> (-) A, R = CH(OH)C <sub>2</sub> H <sub>5</sub> - <i>n</i> (-) A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (-) A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (-) A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (-) n-C <sub>3</sub> H <sub>7</sub> -CH=C=CHSC <sub>2</sub> H <sub>5</sub> (65-70) (CH <sub>3</sub> ) <sub>2</sub> C=C(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )SC <sub>4</sub> H <sub>9</sub> - <i>n</i> (-)	170, 277
	CH <sub>3</sub> S≡CCH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 2.5 hr	CH <sub>3</sub> I  C <sub>2</sub> H <sub>5</sub> Br <i>i</i> -C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> Br CH <sub>3</sub> CHO C <sub>2</sub> H <sub>5</sub> CHO <i>n</i> -C <sub>7</sub> H <sub>15</sub> CHO C <sub>6</sub> H <sub>5</sub> CHO CH <sub>3</sub> COCH <sub>3</sub>	A, R = CH <sub>3</sub> (99) A, R = C <sub>2</sub> H <sub>5</sub> (89) A, R = CH <sub>2</sub> C <sub>2</sub> H <sub>5</sub> - <i>i</i> (80) A, R = CH(OH)CH <sub>3</sub> (-) A, R = CH(OH)C <sub>2</sub> H <sub>5</sub> (-) A, R = CH(OH)C <sub>2</sub> H <sub>5</sub> - <i>n</i> (-) A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (-) A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (-) A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (-) n-C <sub>3</sub> H <sub>7</sub> -CH=C=CHSC <sub>2</sub> H <sub>5</sub> (65-70) (CH <sub>3</sub> ) <sub>2</sub> C=C(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )SC <sub>4</sub> H <sub>9</sub> - <i>n</i> (-)	137 137 137 137 137 137 137 133 110
289	<i>n</i> -C <sub>4</sub> H <sub>9</sub> C≡CSC <sub>2</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> C=CHSC <sub>4</sub> H <sub>9</sub> - <i>n</i>	NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 5 min NaNH <sub>2</sub> (1 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, room temperature, 36 hr	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	n-C <sub>3</sub> H <sub>7</sub> -CH=C=CHSC <sub>2</sub> H <sub>5</sub> (65-70) (CH <sub>3</sub> ) <sub>2</sub> C=C(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )SC <sub>4</sub> H <sub>9</sub> - <i>n</i> (-) + n-C <sub>3</sub> H <sub>7</sub> -C(CH <sub>3</sub> )=CHSC <sub>4</sub> H <sub>9</sub> - <i>n</i> (traces)	133 110
	C <sub>2</sub> H <sub>5</sub> SCH <sub>2</sub> C≡CCH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> ONa (2 eq), NH <sub>3</sub> (liq), 48 hr  <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -50°, 35 min	H <sub>2</sub> O  H <sub>2</sub> O	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )SC <sub>4</sub> H <sub>9</sub> - <i>n</i> (traces) CH <sub>2</sub> =CHC(SC <sub>2</sub> H <sub>5</sub> )=CHSC <sub>2</sub> H <sub>5</sub> (75) + CH <sub>2</sub> =CHC≡CSC <sub>2</sub> H <sub>5</sub> (15) A, CH <sub>2</sub> =C=C=CHSC <sub>2</sub> H <sub>5</sub> + B, CH <sub>2</sub> =CHC≡CSC <sub>2</sub> H <sub>5</sub> A: 80-70, B: 20-30 (60)	182 170, 277
C <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> C≡CH	KOH, THF, 20°, 16 hr KOH (pellets, 2 eq), THF, 55°, 30 min C <sub>2</sub> H <sub>5</sub> ONa (0.1 eq), C <sub>2</sub> H <sub>5</sub> OH, 52°, 5 min NaOH (1.15 eq), C <sub>2</sub> H <sub>5</sub> OH, H <sub>2</sub> O, 35°, 20-30 min	H <sub>2</sub> O - - -	CH <sub>3</sub> C≡CSC <sub>6</sub> H <sub>5</sub> (88) CH <sub>3</sub> C≡CSC <sub>6</sub> H <sub>5</sub> (90)  CH <sub>2</sub> =C=CHSC <sub>6</sub> H <sub>5</sub> (46)  HC≡CCH <sub>2</sub> SC <sub>6</sub> H <sub>5</sub> (17) + CH <sub>2</sub> =C=CHSC <sub>6</sub> H <sub>5</sub> (-) + CH <sub>3</sub> C≡CSC <sub>6</sub> H <sub>5</sub> (-)	579 61, 538  61  536
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, -20°	CH <sub>2</sub> Cl <sub>2</sub> (1 eq), -110° to -120°, warmed to -40° within 3 hr	 (7.5)	238

TABLE XXXVIII. THIOETHERS (Continued)


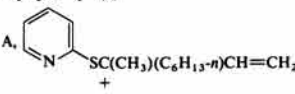
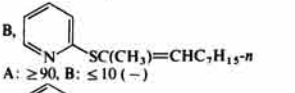

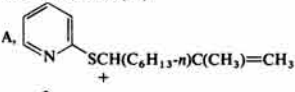
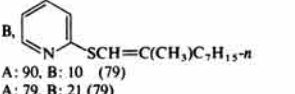
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>9</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> CH=CH <sub>2</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub>	—	CH <sub>2</sub> CH=CHSC <sub>6</sub> H <sub>5</sub> <i>cis</i> : 48, <i>trans</i> : 52 (100)	560
		C <sub>2</sub> H <sub>5</sub> ONa, C <sub>2</sub> H <sub>5</sub> OH, reflux, 12 hr	—	C <sub>6</sub> H <sub>5</sub> SCH=CHCH <sub>3</sub> <i>cis</i> and <i>trans</i> (95)	585
		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )CH=CH <sub>2</sub> (95)	129
		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	A, C <sub>6</sub> H <sub>5</sub> SCH(C <sub>6</sub> H <sub>13-n</sub> )CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> SCH=CHC <sub>7</sub> H <sub>15-n</sub> A: 75, B: 25 (93) A: 68, B: 32 (93)	8 8
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, 5% [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -65°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	C <sub>6</sub> H <sub>5</sub> SCHDCH=CH <sub>2</sub> (69)	220
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 30 min	D <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> SCH=CHCH <sub>3</sub> (71) <i>cis</i> and <i>trans</i> 0 D: 40 1 D: 53 2 D: 8	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -15°, 30 min	CH <sub>3</sub> I	A, C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> SCH=CHC <sub>2</sub> H <sub>5</sub> <i>cis</i> and <i>trans</i> + C, C <sub>6</sub> H <sub>5</sub> SCH=CHCH <sub>3</sub> <i>cis</i> and <i>trans</i> A: 71, B: 22, C: 7 (92)	44, 220
			CH <sub>2</sub> =CHCH <sub>2</sub> Br	A, CH <sub>2</sub> =CHCH(SC <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> SCH=CHCH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> <i>cis</i> and <i>trans</i> + C, C <sub>6</sub> H <sub>5</sub> SCH=CHCH <sub>3</sub> <i>cis</i> and <i>trans</i> A: 62, B: 29, C: 7 (94) A, C <sub>6</sub> H <sub>5</sub> SCH=CHC <sub>2</sub> H <sub>5</sub> + B, C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )CH=CH <sub>2</sub> A (55), (E): 1, (Z): 2, B (44) A (5), (E): 1, (Z): 10, B (88) A (12), (E): 1, (Z): 2, B (83)	44, 220
			CH <sub>3</sub> I		
			Petroleum ether, 25°, 1 hr -78° to 25°, 0.5 hr THF, -78°, 1 hr	0°, neat -78°, THF -78°, neat	
	C <sub>6</sub> H <sub>5</sub> SCH=CHCH <sub>3</sub> ( <i>E</i> ) and ( <i>Z</i> )	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li- <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, 1:1, petroleum ether, 25°, 3.5 hr	CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> SCH=CHCH <sub>3</sub> (33) ( <i>E</i> ) and ( <i>Z</i> ) + C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )CH=CH <sub>2</sub> (1) + C <sub>6</sub> H <sub>5</sub> SCH=CHC <sub>2</sub> H <sub>5</sub> (12) ( <i>E</i> ) and ( <i>Z</i> ) + C <sub>6</sub> H <sub>5</sub> SC(CH <sub>3</sub> )=CHCH <sub>3</sub> (32) ( <i>E</i> ) and ( <i>Z</i> ) + C <sub>6</sub> H <sub>5</sub> SCH <sub>3</sub> (6)	514
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -65°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	A,  + B,  A: ≥90, B: ≤10 (-)	8
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	A,  + B,  A: 90, B: 10 (79) A: 79, B: 21 (79)	8 8
	CH <sub>3</sub> CH=C(C <sub>2</sub> H <sub>5</sub> )C≡CCH <sub>2</sub> SCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, 5% [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, -65° NaNH <sub>2</sub> (1.4 eq), NH <sub>3</sub> (liq), 5 min	H <sub>2</sub> O	A, CH <sub>3</sub> CH=C(C <sub>2</sub> H <sub>5</sub> )C≡CCH <sub>2</sub> SCH <sub>3</sub> + B, CH <sub>3</sub> CH=C(C <sub>2</sub> H <sub>5</sub> )CH=C=CHSCH <sub>3</sub> A: 90, B: 10 (85) A <i>cis</i> : 70, B: 30 (-)	590 590
	CH <sub>3</sub> CH=C(C <sub>2</sub> H <sub>5</sub> )CH=C=CHSCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 30 min	H <sub>2</sub> O		
	CH <sub>3</sub> CH=C(C <sub>2</sub> H <sub>5</sub> )CH=C=CHSCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 120 min	H <sub>2</sub> O	A, CH <sub>3</sub> CH=C(C <sub>2</sub> H <sub>5</sub> )C≡CCH <sub>2</sub> SCH <sub>3</sub> <i>cis</i> + B, CH <sub>3</sub> CH=C(C <sub>2</sub> H <sub>5</sub> )CH=C=CHSCH <sub>3</sub> A: 55, B: 45 (-)	590

TABLE XXXVIII. THIOETHERS (Continued)

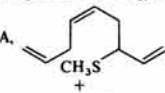
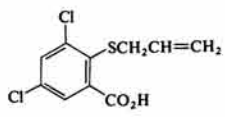
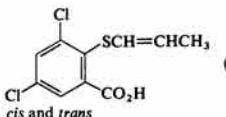
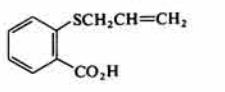
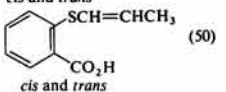

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>9</sub> (Contd.)	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C=CHC≡CSCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> ONa (0.5 eq), NH <sub>3</sub> (liq), 420 min	H <sub>2</sub> O	A, CH <sub>3</sub> CH=C(C <sub>2</sub> H <sub>5</sub> )C≡CCH <sub>2</sub> SCH <sub>3</sub> <i>cis</i>	590
		NaNH <sub>2</sub> (1.4 eq), NH <sub>3</sub> (liq), 5 min	H <sub>2</sub> O	B, CH <sub>3</sub> CH=C(C <sub>2</sub> H <sub>5</sub> )CH=C=CHSCH <sub>3</sub> + C, (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C=CHC≡CSCH <sub>3</sub> A: 30, B: 20, C: 50 (-) CH <sub>3</sub> CH=C(C <sub>2</sub> H <sub>5</sub> )CH=C=CHSCH <sub>3</sub> (50)	590
	HC≡CCH <sub>2</sub> SCH(C <sub>2</sub> H <sub>5</sub> )C(CH <sub>3</sub> )=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, -78°	CH <sub>3</sub> I (2 eq)	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C=CHC≡CH (35) CH <sub>3</sub> C≡CCH(SCH <sub>3</sub> )CH <sub>2</sub> C(CH <sub>3</sub> )=CHC <sub>2</sub> H <sub>5</sub> (82)	483
292	CH <sub>2</sub> =CHCH(SCH <sub>2</sub> CH=CH <sub>2</sub> )CH <sub>2</sub> CH=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -18°, 1 hr	CH <sub>3</sub> I	A,  + B, 	216
	C <sub>2</sub> H <sub>5</sub> SCH <sub>2</sub> C≡CCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> ONa (1 eq), NH <sub>3</sub> (liq), 48 hr	H <sub>2</sub> O	A: 75, B: 25 (97) CH <sub>3</sub> CH=CHC≡CSC <sub>2</sub> H <sub>5</sub> (72) + C <sub>2</sub> H <sub>5</sub> SCH <sub>2</sub> C≡CCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> (15)	182
	<i>i</i> -C <sub>3</sub> H <sub>7</sub> SCH <sub>2</sub> C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> ONa (1 eq), NH <sub>3</sub> (liq), 48 hr	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> SCH=C=CHCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub> (-) CH <sub>2</sub> =CHC≡CSC <sub>3</sub> H <sub>7-<i>i</i></sub> (76) + <i>i</i> -C <sub>3</sub> H <sub>7</sub> SCH <sub>2</sub> C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> (15)	182
	CH <sub>2</sub> =CHCH <sub>2</sub> SCH(C <sub>2</sub> H <sub>5</sub> )C(CH <sub>3</sub> )=CH <sub>2</sub> CH <sub>2</sub> =CHCH(C <sub>4</sub> H <sub>9-<i>n</i></sub> )SC <sub>2</sub> H <sub>5</sub>	NaNH <sub>2</sub> , NH <sub>3</sub> (liq), 30 min <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> , 50°, 30 min KNH <sub>2</sub> , CH <sub>3</sub> SOCH <sub>3</sub> , 50°, 30 min	CH <sub>3</sub> I - H <sub>2</sub> O	<i>i</i> -C <sub>3</sub> H <sub>7</sub> SCH=C=CHCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> (-) CH <sub>2</sub> =CHCH(SCH <sub>3</sub> )CH <sub>2</sub> C(CH <sub>3</sub> )=CHC <sub>2</sub> H <sub>5</sub> (81) CH <sub>3</sub> CH=C(C <sub>4</sub> H <sub>9-<i>n</i></sub> )SC <sub>2</sub> H <sub>5</sub> <i>cis</i> : 1, <i>trans</i> : 1 (60-62) CH <sub>3</sub> CH=C(C <sub>4</sub> H <sub>9-<i>n</i></sub> )SC <sub>2</sub> H <sub>5</sub> (60-66)	483 352 352
	CH <sub>2</sub> =CHCH <sub>2</sub> SC <sub>6</sub> H <sub>13-<i>n</i></sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> ONa (1 eq), 60°, 21 hr	-	CH <sub>3</sub> CH=CHSC <sub>6</sub> H <sub>13-<i>n</i></sub> <i>cis</i> : 59, <i>trans</i> : 41 (69.2) <i>cis</i> and <i>trans</i> (61)	540 217
C <sub>10</sub>		10% NaOH, reflux, 12 hr	-	 (50) <i>cis</i> and <i>trans</i>	585
		10% NaOH, reflux 15 hr	-	 (50) <i>cis</i> and <i>trans</i>	585
	HC≡CCH(CH <sub>3</sub> )SC <sub>6</sub> H <sub>5</sub>	KOH (4 eq), THF, 20°, 10 min KOH (pellets) (2 eq), THF, room temperature, 15 min	-	CH <sub>2</sub> =C=C(CH <sub>3</sub> )SC <sub>6</sub> H <sub>5</sub> (67) + HC≡CCH(CH <sub>3</sub> )SC <sub>6</sub> H <sub>5</sub> (2) CH <sub>2</sub> =C=C(CH <sub>3</sub> )SC <sub>6</sub> H <sub>5</sub> (67)	536 61, 538
	C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> CH=CClCH <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -80° to -30°	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	C <sub>6</sub> H <sub>5</sub> SCH(C <sub>4</sub> H <sub>9-<i>n</i></sub> )CH=CClCH <sub>3</sub> (-)	244
293	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S 	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30° to -20°, 30 min	CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> CHRS 	429 429 429, 525 429 447 447 216
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SCH <sub>2</sub> CH=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -78°, 1 hr	CH <sub>3</sub> I	A, R = CH <sub>3</sub> (60) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (45) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (45) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3-<i>p</i></sub> (34) A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> (80) A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (100) A, C <sub>6</sub> H <sub>5</sub> CH(SCH <sub>3</sub> )CH <sub>2</sub> CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SCH(CH <sub>3</sub> )CH=CH <sub>2</sub> + C, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SCH=CHC <sub>2</sub> H <sub>5</sub> <i>cis</i> and <i>trans</i> A: 23, B: 76, C: 1 (98) A, C <sub>6</sub> H <sub>5</sub> CH(SCH <sub>3</sub> )CH <sub>2</sub> CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH=CHSCH <sub>3</sub> <i>trans</i> + C, CH <sub>3</sub> SCH=CHCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3-<i>p</i></sub> <i>trans</i> A: 67, B: 6, C: 27 (97)	216

TABLE XXXVIII. THIOETHERS (Continued)

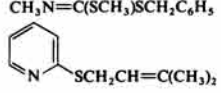

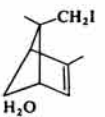
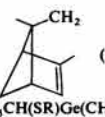
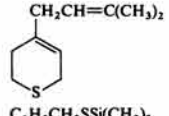

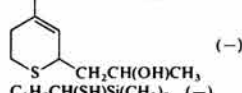
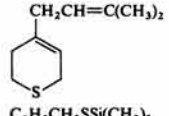
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>10</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )CH=CH <sub>2</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, 0°, 30 min	CH <sub>3</sub> I	A, C <sub>6</sub> H <sub>5</sub> SC(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> SC(CH <sub>3</sub> )=CHC <sub>2</sub> H <sub>5</sub> <i>cis</i> and <i>trans</i> A: 70, B: 30 (99)	220	
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub>	—	CH <sub>3</sub> CH=C(CH <sub>3</sub> )SC <sub>6</sub> H <sub>5</sub> ( <i>E</i> ): 46, ( <i>Z</i> ): 54 (—)	560	
	C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -15°, 30 min	CH <sub>3</sub> I	A, C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )C(CH <sub>3</sub> )=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> SCH=C(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub> <i>cis</i> and <i>trans</i> + C, C <sub>6</sub> H <sub>5</sub> SCH=C(CH <sub>3</sub> ) <sub>2</sub> A: 80, B: 13, C: 7 (91)	220	
		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	A, C <sub>6</sub> H <sub>5</sub> SCH(C <sub>6</sub> H <sub>13</sub> - <i>n</i> )C(CH <sub>3</sub> )=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> SCH=C(CH <sub>3</sub> )C <sub>7</sub> H <sub>15</sub> - <i>n</i> A: 75, B: 25 (84) A: 70, B: 30 (84)	8 8	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li: [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 95:5, THF, -65° <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> , <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , -75°, then 23°, 15 hr	<i>n</i> -C <sub>6</sub> H <sub>13</sub> I, -65°	CH <sub>3</sub> I	(CH <sub>3</sub> ) <sub>2</sub> C=CHSC <sub>6</sub> H <sub>5</sub> (100) C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )SCH=CHCH <sub>3</sub> <i>cis</i> and <i>trans</i> (—)	560 202
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SCH=CHCH <sub>3</sub> <i>cis</i> and <i>trans</i> C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> CH=CHCH <sub>3</sub> <i>trans</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -15°, 30 min	CH <sub>3</sub> I	A, C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )CH=CHCH <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> SCH=CHC <sub>2</sub> H <sub>5</sub> + C, C <sub>6</sub> H <sub>5</sub> SCH=CHC <sub>2</sub> H <sub>5</sub> A: 98, B + C: 2 (92)	220	
		CH <sub>3</sub> N=C(SCH <sub>3</sub> )SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	LDA, THF, -78°	(CH <sub>3</sub> ) <sub>3</sub> SiCl	CH <sub>3</sub> N=C(SCH <sub>3</sub> )SCH(C <sub>6</sub> H <sub>5</sub> )Si(CH <sub>3</sub> ) <sub>3</sub> (—)	24
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -70°, 30 min	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> Br		 A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (89) A, R = CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (77)	300 300
	C <sub>10</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SGe(CH <sub>3</sub> ) <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 0.8 hr	 H <sub>2</sub> O	A, R =  (79)	300
				CH <sub>3</sub> I (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiCl	A, C <sub>6</sub> H <sub>5</sub> CH(SR)Ge(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SR A: 75, B: 25, R = H (—) A: 72, B: 26, R = CH <sub>3</sub> (—) A: 72, B: 28, R = Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (—)	608 608 608
		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SSi(CH <sub>3</sub> ) <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA, -50°, 2 hr	CH <sub>3</sub> CHCH <sub>2</sub> 	 (—)	481
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 0.01 hr	H <sub>2</sub> O CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> CH(SH)Si(CH <sub>3</sub> ) <sub>3</sub> (—) A, C <sub>6</sub> H <sub>5</sub> CH[Si(CH <sub>3</sub> ) <sub>3</sub> ]SCH <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SCH <sub>3</sub> + C, C <sub>6</sub> H <sub>5</sub> CH(SCH <sub>3</sub> )Si(CH <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> H <sub>5</sub> A: 86, B: 2, C: 12 (—) A: 87, B: 3, C: 11 (—) A, C <sub>6</sub> H <sub>5</sub> CH[Si(CH <sub>3</sub> ) <sub>3</sub> ]SSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH[SSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ]Si(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> A: 90, B: 10 (—) C <sub>6</sub> H <sub>5</sub> CH(SH)Si(CH <sub>3</sub> ) <sub>3</sub> (90)	608 608 608
		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SSi(CH <sub>3</sub> ) <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), THF, -78°	H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH(SH)Si(CH <sub>3</sub> ) <sub>3</sub> (90) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SH (0.4)	47
				CH <sub>3</sub> I	A, C <sub>6</sub> H <sub>5</sub> CH(SCH <sub>3</sub> )Si(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH(SCH <sub>3</sub> )Si(CH <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> H <sub>5</sub> + C, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SCH <sub>3</sub> A: 93, B: 7, C: 0.1 (—)	47
				(CH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiCl	A: 94, B: 4, C: 2 (—) A, C <sub>6</sub> H <sub>5</sub> CH[SSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ]Si(CH <sub>3</sub> ) <sub>3</sub> + B, C <sub>6</sub> H <sub>5</sub> CH[SSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ]Si(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> A: 90, B: 10 (—) CH <sub>2</sub> =CHC≡CSC <sub>6</sub> H <sub>5</sub> - <i>t</i> (72)	47 47
<i>t</i> -C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>		C <sub>2</sub> H <sub>5</sub> ONa (1 eq), NH <sub>3</sub> (liq), 48 hr	H <sub>2</sub> O	<i>t</i> -C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> C≡CCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> (18) + <i>t</i> -C <sub>4</sub> H <sub>9</sub> SCH=C=CHCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> (—)	182	

TABLE XXXVIII. THIOETHERS (Continued)


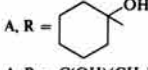
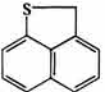
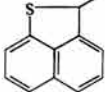


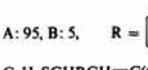

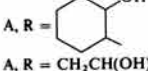


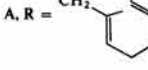
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>11</sub> (Contd.)	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SC(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 4 hr	H <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> CHSRCH=C(CH <sub>3</sub> ) <sub>2</sub> A, R = H (100)	180
			CH <sub>3</sub> I	A, R = CH <sub>3</sub> (100)	180
	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SCH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 4 hr	H <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH(SR)C(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub> A, R = H (100)	180
			CH <sub>3</sub> I	A, R = CH <sub>3</sub> (100)	180
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -15° or 25°, 1 hr	CH <sub>3</sub> I	A, R = CH <sub>3</sub> (94)	216
			CH <sub>3</sub> I		
	<i>i</i> -C <sub>3</sub> H <sub>7</sub> SCH <sub>2</sub> C≡CCH <sub>2</sub> SC <sub>3</sub> H <sub>7</sub> - <i>i</i>	C <sub>2</sub> H <sub>5</sub> ONa (2 eq), NH <sub>3</sub> (liq), 48 hr	H <sub>2</sub> O	CH <sub>2</sub> =CHC(SC <sub>3</sub> H <sub>7</sub> - <i>i</i> )=CHSC <sub>3</sub> H <sub>7</sub> - <i>i</i> (50)	182
	<i>t</i> -C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> C≡CSi(CH <sub>3</sub> ) <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li	(CH <sub>3</sub> ) <sub>3</sub> SiCl	CH <sub>2</sub> =CHC≡CSC <sub>3</sub> H <sub>7</sub> - <i>t</i> (39)	497
			CH <sub>3</sub> I	<i>t</i> -C <sub>4</sub> H <sub>9</sub> SCHRC≡CSi(CH <sub>3</sub> ) <sub>3</sub> A, R = Si(CH <sub>3</sub> ) <sub>3</sub> (80)	497
			C <sub>2</sub> H <sub>5</sub> Br	A, R = CH <sub>3</sub> (85)	497
		<i>i</i> -C <sub>3</sub> H <sub>7</sub> CHO	A, R = C <sub>2</sub> H <sub>5</sub> (80)	497	
		<i>t</i> -C <sub>4</sub> H <sub>9</sub> CHO	A, R = CH(OH)C <sub>3</sub> H <sub>7</sub> - <i>i</i> (78)	497	
		CH <sub>3</sub> COCH <sub>3</sub>	A, R = CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>t</i> (70)	497	
			A, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (93)	497	
			A, R =  (83)	497	
		C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	A, R = C(OH)(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (65)	497	
C <sub>11</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -60°, 5 min	CH <sub>3</sub> I	 (83)	405
	C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 30 min	D <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> SCHDCH=C(CH <sub>3</sub> ) <sub>2</sub> (98)	44, 220
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -15°, 30 min	CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )CH=C(CH <sub>3</sub> ) <sub>2</sub> (98)	44, 220
			CH <sub>2</sub> =CHCH <sub>2</sub> Br	A, C <sub>6</sub> H <sub>5</sub> SCH(R)CH=C(CH <sub>3</sub> ) <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> SCH=CHCR(CH <sub>3</sub> ) <sub>2</sub> <i>trans</i>	
			(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Br	A: 87, B: 13, R = CH <sub>2</sub> CH=CH <sub>2</sub> (89) A: 91, B: 6, R = CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	44, 220 44, 220
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>3</sub> COCH <sub>3</sub>	A: 25, B: 75, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (100)	279
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -78°, 30 min		A: trace, B: 90, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (100)	279
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -20°, 30 min		A: 0, B: 100, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (100)	279
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, THF, -78°, 30 min	CH <sub>3</sub> I	A: 98, B: trace, R = CH <sub>3</sub> (100)	279
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 30 min	CH <sub>3</sub> COCH <sub>3</sub> CH <sub>3</sub> I	A: 40, B: 60, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (100) A: 60, B: 40, R = CH <sub>3</sub> (80)	279 279
		CH <sub>2</sub> =CHCH <sub>2</sub> Br CH <sub>3</sub> COCH <sub>3</sub>	A: 50, B: 50, R = CH <sub>2</sub> CH=CH <sub>2</sub> (60) C <sub>6</sub> H <sub>5</sub> SCH[C(OH)(CH <sub>3</sub> ) <sub>2</sub> ]CH=C(CH <sub>3</sub> ) <sub>2</sub> (60) + C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub> (-) A, C <sub>6</sub> H <sub>5</sub> SCH=CHC(CH <sub>3</sub> ) <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )CH=C(CH <sub>3</sub> ) <sub>2</sub> A (21), B (77) A (1), B (98)	279 279	
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li- <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, 1:1 (1.1 eq), petroleum ether, 25°, 1 hr, -78° to 25°, 0.5 hr, then 25°, 1 hr	0°, neat -78° THF	C <sub>2</sub> H <sub>5</sub> CHO	C <sub>2</sub> H <sub>5</sub> CH(OH)C(CH <sub>3</sub> ) <sub>2</sub> CH=CHSC <sub>6</sub> H <sub>5</sub> (85)	89 89 315
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 2 hr	C <sub>6</sub> H <sub>5</sub> CHO CH <sub>3</sub> COCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH(OH)C(CH <sub>3</sub> ) <sub>2</sub> CH=CHSC <sub>6</sub> H <sub>5</sub> (92) A, R(CH <sub>3</sub> ) <sub>2</sub> CH=CHSC <sub>6</sub> H <sub>5</sub> + B, (CH <sub>3</sub> ) <sub>2</sub> C=CHCHRSC <sub>6</sub> H <sub>5</sub> A: 91, B: 9, R = C(OH)(CH <sub>3</sub> ) <sub>2</sub> (70)	315 315	
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA, -50°, then 20°, 2 hr	 ClCH <sub>2</sub> (CH <sub>3</sub> )C=CHCH <sub>2</sub> OTHP ( <i>E</i> ) CH <sub>3</sub> CHCH <sub>2</sub> 		A: 95, B: 5, R =  (85)	315
				C <sub>6</sub> H <sub>5</sub> SCHRCH=C(CH <sub>3</sub> ) <sub>2</sub> A, R = CH <sub>2</sub> (CH <sub>3</sub> )C=CHCH <sub>2</sub> OTHP (-) A, R = CH <sub>2</sub> CH(OH)CH <sub>3</sub> (82)	480 241
				A, R =  (-)	241
		C <sub>6</sub> H <sub>5</sub> CHCH <sub>2</sub> 		A, R = CH <sub>2</sub> CH(OH)C <sub>6</sub> H <sub>5</sub> (-)	241
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -20°, 30 min	 CH <sub>2</sub> OTHP CH <sub>2</sub> Br		A, R =  (51)	524

TABLE XXXVIII. THIOETHERS (Continued)

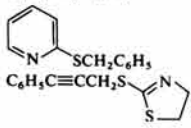


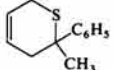
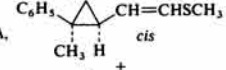
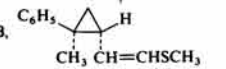
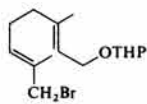
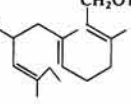
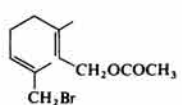
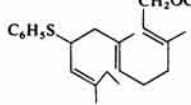
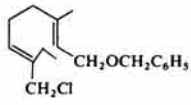
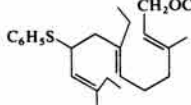
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>11</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )C(CH <sub>3</sub> )=CH <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, 0°	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I <i>n</i> -C <sub>4</sub> H <sub>9</sub> I CH <sub>3</sub> COCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> SC(CH <sub>3</sub> )(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )C(CH <sub>3</sub> )=CH <sub>2</sub> (-) C <sub>6</sub> H <sub>5</sub> SC(CH <sub>3</sub> )(C <sub>4</sub> H <sub>9</sub> - <i>n</i> )C(CH <sub>3</sub> )=CH <sub>2</sub> (49) A, C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )C(CH <sub>3</sub> )=CH <sub>2</sub> + B, C <sub>6</sub> H <sub>5</sub> SC(CH <sub>3</sub> )[(CH <sub>3</sub> ) <sub>2</sub> C(OH)]C(CH <sub>3</sub> )=CH <sub>2</sub> + C, C <sub>6</sub> H <sub>5</sub> SC(CH <sub>3</sub> )=C(CH <sub>3</sub> )CH <sub>2</sub> C(OH)(CH <sub>3</sub> ) A (12), B (51), C (18) C <sub>6</sub> H <sub>5</sub> SCH=C(CH <sub>3</sub> )CH(CH <sub>3</sub> )C(OH)(CH <sub>3</sub> ) <sub>2</sub> (72) C <sub>6</sub> H <sub>5</sub> CHDSC <sub>4</sub> H <sub>9</sub> - <i>t</i> (-)	294 626 626
C <sub>12</sub> 298	C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SC <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, 0° <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 2 hr	CH <sub>3</sub> COCH <sub>3</sub> D <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>3</sub> (71)	626 180
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 10 min	C <sub>6</sub> H <sub>5</sub> CHO, -78°, 3 hr, then H <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CHCHC≡CC <sub>6</sub> H <sub>5</sub> (20) <i>cis</i> and <i>trans</i> + C <sub>6</sub> H <sub>5</sub> CH=CHC≡CC <sub>6</sub> H <sub>5</sub> (20) <i>cis</i> and <i>trans</i>	447
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, -60°, 20 min	CH <sub>3</sub> I  HC≡CCH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> C≡CCH <sub>2</sub> Br	A, R = CH <sub>3</sub> (45) A, R = CH <sub>2</sub> C≡CH (45) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (50) A, R = CH <sub>2</sub> C≡CC <sub>6</sub> H <sub>5</sub> (50)	430 430 430 430
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), THF, -60°	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> CHCHC≡CC <sub>6</sub> H <sub>5</sub> (20) <i>cis</i> and <i>trans</i> + C <sub>6</sub> H <sub>5</sub> CH=CHC≡CC <sub>6</sub> H <sub>5</sub> (20) <i>cis</i> and <i>trans</i>	247
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -60°	HC≡CCH <sub>2</sub> Br  C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> C≡CCHRS A, R = CH <sub>2</sub> C≡CH (45) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (50) C <sub>6</sub> H <sub>5</sub> CHCHC≡CC <sub>6</sub> H <sub>5</sub> (-)	311 311 311
	C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> S 	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -60°, 30 min	CH <sub>3</sub> I  <i>i</i> -C <sub>3</sub> H <sub>7</sub> Br C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> CH=CHCHRS  A, R = CH <sub>3</sub> (47) A, R = C <sub>2</sub> H <sub>5</sub> - <i>i</i> (10) A, R = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (45) A, R = CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (30)	429 429 311, 429 311, 429
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -15°, 1 hr	CH <sub>3</sub> I	A,  <i>cis</i> + B,  <i>cis</i>	219
	C <sub>6</sub> H <sub>5</sub> C≡CCH(CH <sub>3</sub> )SC <sub>2</sub> H <sub>5</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> <i>i</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub>	- -	A: 50, B: 50 (97) C <sub>6</sub> H <sub>5</sub> CH=C=C(CH <sub>3</sub> )SC <sub>2</sub> H <sub>5</sub> (-) C <sub>6</sub> H <sub>5</sub> CH=C=C(CH <sub>3</sub> )SC <sub>2</sub> H <sub>5</sub> (70) CH <sub>2</sub> OTHP	509 494
	C <sub>2</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> SC <sub>6</sub> H <sub>5</sub> ( <i>Z</i> )	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, DABCO, -15°, 40 min		C <sub>6</sub> H <sub>5</sub> S  (58)	511, 512
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°		C <sub>6</sub> H <sub>5</sub> S  (-)	416
				C <sub>6</sub> H <sub>5</sub> S  (75)	591
	CH <sub>2</sub> =CHC(CH <sub>3</sub> ) <sub>2</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 5 hr	CH <sub>3</sub> I H <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> CH(SCH <sub>2</sub> )C <sub>6</sub> H <sub>5</sub> (100)	180
	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 1.5 hr -30°, 9 min	CH <sub>3</sub> I H <sub>2</sub> O D <sub>2</sub> O	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> CH(SH)C <sub>6</sub> H <sub>5</sub> (100) CH <sub>2</sub> =CHC(CH <sub>3</sub> ) <sub>2</sub> CH(SH)C <sub>6</sub> H <sub>5</sub> (100) CH <sub>2</sub> =CHC(CH <sub>3</sub> ) <sub>2</sub> CH(SH)C <sub>6</sub> H <sub>5</sub> (-) A, CH <sub>2</sub> =CHC(CH <sub>3</sub> ) <sub>2</sub> CH(SH)C <sub>6</sub> H <sub>5</sub> + B, (CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> A: 1, B: 2, no deuterium (-)	180 180 180 180

TABLE XXXVIII. THIOETHERS (Continued)

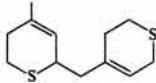
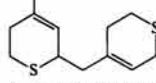
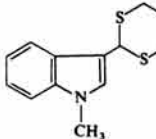
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>12</sub> (Contd.)	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -15°, 1 hr	CH <sub>3</sub> I	C <sub>6</sub> H <sub>5</sub> CH(SCH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub> CH=CH <sub>2</sub> (97)	216
	C <sub>6</sub> H <sub>5</sub> SCH=C(CH <sub>3</sub> )CH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	LDA, THF, -78°, 15-25 min	C <sub>6</sub> H <sub>5</sub> CHO, -78°, 15 min C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHO, -78°, 45 min	C <sub>6</sub> H <sub>5</sub> SCH=C(CH <sub>3</sub> )CH(SC <sub>2</sub> H <sub>5</sub> )CH(OH)C <sub>6</sub> H <sub>5</sub> (100) C <sub>6</sub> H <sub>5</sub> SCH=C(CH <sub>3</sub> )CH(SC <sub>2</sub> H <sub>5</sub> )CH(OH)CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (89)	584 584
300		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -20°	ClCH <sub>2</sub> (CH <sub>3</sub> )C=CHCH <sub>2</sub> OTHP (E)  CH <sub>3</sub> CHCH <sub>2</sub>   O	 A, R = CH <sub>2</sub> (CH <sub>3</sub> )C=CHCH <sub>2</sub> OTHP (60) A, R = CH <sub>2</sub> CH(OH)CH <sub>3</sub> (84)	479 479
	C <sub>2</sub> H <sub>5</sub> SCH <sub>2</sub> C≡CC(CH <sub>3</sub> ) <sub>2</sub> OCH(CH <sub>3</sub> )OC <sub>2</sub> H <sub>5</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li (1 eq), THF, TMEDA (3 eq), 5° C <sub>2</sub> H <sub>5</sub> ONa (1 eq), NH <sub>3</sub> (liq), 48 hr	H <sub>2</sub> O	A, R = CH <sub>2</sub> (CH <sub>3</sub> )C=CHCH <sub>2</sub> OH (>90)  (CH <sub>3</sub> ) <sub>2</sub> C=CHC≡CSC <sub>2</sub> H <sub>5</sub> (62)  CH <sub>2</sub> =C(CH <sub>3</sub> )CH=C=C(SC <sub>2</sub> H <sub>5</sub> )CH(OH)CH <sub>3</sub> (28) C <sub>2</sub> H <sub>5</sub> SCH=C(CH <sub>3</sub> ) <sub>2</sub> CH(SH)CH=C(CH <sub>3</sub> ) <sub>2</sub> <i>trans</i> (35)	130 182
	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> SCH(SC <sub>2</sub> H <sub>5</sub> )CH=C(CH <sub>3</sub> ) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -15°, 45 min	H <sub>2</sub> O	CH <sub>2</sub> =CHC(SC <sub>4</sub> H <sub>9</sub> - <i>t</i> )=CHSC <sub>4</sub> H <sub>9</sub> - <i>t</i> (15)  CH <sub>2</sub> =CHC≡CSC <sub>4</sub> H <sub>9</sub> - <i>t</i> (65) A, CH <sub>2</sub> =C=C=CHSC <sub>4</sub> H <sub>9</sub> - <i>t</i>  B, CH <sub>2</sub> =CC≡CSC <sub>4</sub> H <sub>9</sub> - <i>t</i> A: 1, B: 9 (30)	490 182
	<i>t</i> -C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> C≡CC <sub>2</sub> H <sub>5</sub> SC <sub>4</sub> H <sub>9</sub> - <i>t</i>	C <sub>2</sub> H <sub>5</sub> ONa (2 eq), NH <sub>3</sub> (liq), 48 hr	H <sub>2</sub> O		170
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), ether, -50°, 35 min	H <sub>2</sub> O		
C <sub>13</sub>	C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, 0°, 30 min	CH <sub>3</sub> I  CH <sub>2</sub> =CHCH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (98)  A, C <sub>6</sub> H <sub>5</sub> SCH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH=CH <sub>2</sub>  B, C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> A: 89, B: 11 (92) C <sub>6</sub> H <sub>5</sub> CH(CO <sub>2</sub> H)SC <sub>6</sub> H <sub>5</sub> (75) C <sub>6</sub> H <sub>5</sub> SCH(C <sub>6</sub> H <sub>5</sub> )CH(OH)C <sub>6</sub> H <sub>5</sub> (56) <i>threo</i> : 60, <i>erythro</i> : 40  C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH (-)	44, 220 44, 220
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, ether, reflux, 5 hr C <sub>6</sub> H <sub>5</sub> Li, ether, reflux, 0.25 hr	CO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CHO		53 472
	C <sub>6</sub> H <sub>5</sub> C≡CCH(C <sub>2</sub> H <sub>5</sub> )SC <sub>2</sub> H <sub>5</sub> <i>n</i> -C <sub>9</sub> H <sub>19</sub> CH=CHCH <sub>2</sub> SCH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub> <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, CH <sub>3</sub> SOCH <sub>3</sub> , room temperature, 30 min	- -	C <sub>6</sub> H <sub>5</sub> CH=C=C(C <sub>2</sub> H <sub>5</sub> )SC <sub>2</sub> H <sub>5</sub> (60) A, <i>n</i> -C <sub>9</sub> H <sub>19</sub> CH <sub>2</sub> CH=CHSCH <sub>3</sub> <i>cis</i> : 27, <i>trans</i> : 40  B, <i>n</i> -C <sub>9</sub> H <sub>19</sub> CH=CHCH <sub>2</sub> SCH <sub>3</sub> A: 67, B: 33 (-)	494 522
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -20°, 5 hr	CH <sub>3</sub> I, -20° to room temperature,	(53)	582
	<i>t</i> -C <sub>4</sub> H <sub>9</sub> SCH[Si(CH <sub>3</sub> ) <sub>3</sub> ]C≡CSi(CH <sub>3</sub> ) <sub>3</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li	CH <sub>3</sub> I	A, <i>t</i> -C <sub>4</sub> H <sub>9</sub> SC(CH <sub>3</sub> ) <sub>3</sub> [Si(CH <sub>3</sub> ) <sub>3</sub> ]C≡CSi(CH <sub>3</sub> ) <sub>3</sub>  B, <i>t</i> -C <sub>4</sub> H <sub>9</sub> Si[Si(CH <sub>3</sub> ) <sub>3</sub> ]=C=C(CH <sub>3</sub> )Si(CH <sub>3</sub> ) <sub>3</sub> A: 30, B: 70 (65)	497
C <sub>14</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, (CH <sub>3</sub> ) <sub>2</sub> NCHO, 80° <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (3 eq), (CH <sub>3</sub> ) <sub>2</sub> NCHO, 80°, 20 hr	- -	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (41) <i>cis</i> : 1, <i>trans</i> : 13 C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (45)  H <sub>2</sub> S (-) A, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(SCH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>  B, <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH(SCH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> A: 100, B: 0 (-) A: 100, B: 0 (-)	599 598
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA (1 eq), C <sub>6</sub> H <sub>12</sub> , 11°, 45 min	CH <sub>3</sub> I		223 223
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA (15 eq), LiBr (14 eq), THF, 11°, 45 min			
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, 11°, 45 min			
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA (1 eq), THF, 11°, 45 min			
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA (1 eq), THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 50:1, 11°, 45 min			
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, [2.2.2] (1 eq), THF, 11°, 45 min			
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA (1 eq), LiBr (9 eq), THF, 11°, 45 min			
		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NLi, ether-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 1:1, -10°, 30°, 20 hr			
		KNH <sub>2</sub> , NH <sub>3</sub> (liq), ether, room temperature, 1.5 hr, then reflux, 16 hr			
				C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (45)	550
				C <sub>6</sub> H <sub>5</sub> CH(SH)C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> (79)	222



TABLE XXXVIII. THIOETHERS (Continued)

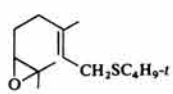
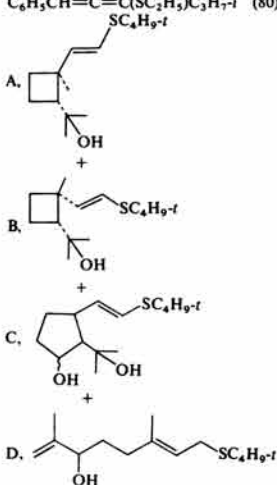
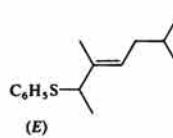
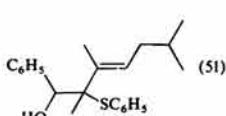
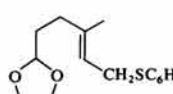
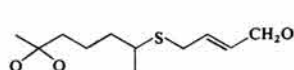
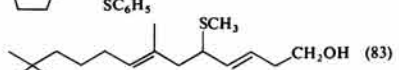
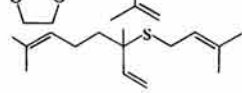

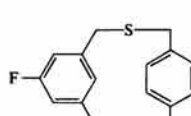
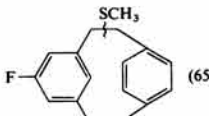
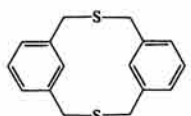
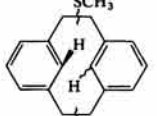
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>14</sub> (Contd.)	<chem>C6H5CH2SSCH2C6H5</chem>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, (CH <sub>3</sub> ) <sub>2</sub> NCHO, 80°	—	<chem>C6H5CH=CHC6H5</chem> (13-17) +	598, 599
	<chem>C6H5C#CC(SC2H5)C3H7-i</chem>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub>	—	H <sub>2</sub> S (8-10) <chem>C6H5CH=C=C(SC2H5)C3H7-i</chem> (80)	494
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (5 eq), TMEDA (5 eq), THF- <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 2.4:1, -75°, 3 hr, then 5°, 2 hr		A, B, C, D 	327a
C <sub>15</sub>	<chem>C6H5SCH2CH=CHSC6H5</chem>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -20°, 45 min	CH <sub>3</sub> I <i>i</i> -C <sub>4</sub> H <sub>9</sub> I	A: 43, B: 29, C: 25, D: 3 (64) <chem>C6H5SCH(CH3)CH=CHSC6H5</chem> (98) <chem>C6H5SCH(i-C4H9)CH=CHSC6H5</chem> (98)	372 372
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, 0°, 1 hr, CdI <sub>2</sub> , 10 min	C <sub>6</sub> H <sub>5</sub> CHO	 (51)	626
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	<i>m</i> -i-C <sub>3</sub> H <sub>7</sub> , C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	(-)	627
		NaNH <sub>2</sub> , NH <sub>3</sub> (liq)	CH <sub>3</sub> I	 (83)	483
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -30°, 5 hr	CH <sub>3</sub> I	 CH <sub>2</sub> CH(SCH <sub>3</sub> )CH=C(CH <sub>3</sub> ) <sub>2</sub>	180
	<chem>HC#CCH2SC12H25-n</chem>	KOH (pellets, 2 eq), THF, room temperature, 3 hr	—	<i>cis</i> and <i>trans</i> (87) <chem>CH3C#CSC12H25-n</chem> (72)	61, 538
C <sub>16</sub>		LDA (2.5 eq), THF, 0°	CH <sub>3</sub> I	 (65)	508
		LDA (2.5 eq), THF, 0°	CH <sub>3</sub> I	 <i>anti</i> : 70, <i>syn</i> : 30 (94)	508

TABLE XXXVIII. THIOETHERS (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>16</sub> (Contd.)		LDA (2.5 eq), THF, 0°	CH <sub>3</sub> I	 (65)	508
		LDA (2.5 eq), THF, 0°	CH <sub>3</sub> I	 (24)	508
	C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> C(CH <sub>3</sub> )=CHSC <sub>6</sub> H <sub>5</sub>	sec-C <sub>4</sub> H <sub>9</sub> Li, THF, -20°, 45 min	CH <sub>3</sub> I n-C <sub>4</sub> H <sub>9</sub> I	C <sub>6</sub> H <sub>5</sub> SCH(R)C(CH <sub>3</sub> )=CHSC <sub>6</sub> H <sub>5</sub> A, R = CH <sub>3</sub> (94) A, R = C <sub>4</sub> H <sub>9</sub> -n (98)	372 372
	C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )CH=CHSC <sub>6</sub> H <sub>5</sub> or C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> CH=C(CH <sub>3</sub> )SC <sub>6</sub> H <sub>5</sub>	sec-C <sub>4</sub> H <sub>9</sub> Li, THF, -20°, 45 min	 CH <sub>3</sub> I	A, R = (94) A, C <sub>6</sub> H <sub>5</sub> SC(CH <sub>3</sub> ) <sub>2</sub> CH=CHCH(CH <sub>3</sub> )SC <sub>6</sub> H <sub>5</sub> + B, C <sub>6</sub> H <sub>5</sub> SC(CH <sub>3</sub> ) <sub>2</sub> CH=CHSC <sub>6</sub> H <sub>5</sub> A: 9, B: 1 (98)	372 372
	C <sub>6</sub> H <sub>5</sub> C≡CCH(SC <sub>2</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub> -n	t-C <sub>4</sub> H <sub>9</sub> OK (cat), CH <sub>3</sub> SOCH <sub>3</sub>	-	C <sub>6</sub> H <sub>5</sub> CH=C=C(SC <sub>2</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub> -n (65)	494
304		n-C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -18°, 30 min		 (60) +  (12)	87, 295
				 (58) +  (11)	87, 295
		n-C <sub>4</sub> H <sub>9</sub> Li, THF, -78°, 1.5-2.5 hr		 (76)	296, 327
		n-C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF, -50°, then -20°, 2 hr	CH <sub>3</sub> CHCH <sub>2</sub> 	 (-)  (-)	297 241
305			CICH <sub>2</sub> (CH <sub>3</sub> )C=CHCH <sub>2</sub> OTHP (E)	 (-)	480

TABLE XXXVIII. THIOETHERS (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>16</sub> (Contd.)		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -18°, 30 min		 (71) +  (14)	87, 295
306 C <sub>17</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -15°, 1 hr	CH <sub>3</sub> I	 (95) <i>cis</i>	219
		-78°, 1 hr	CH <sub>3</sub> I	 (95.5)	219
C <sub>18</sub>		<i>sec</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -20°, 45 min	CH <sub>3</sub> I	 (90)	372
			C <sub>6</sub> H <sub>5</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub>	 CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (95)	372
	(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> SC <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, DABCO (1.1 eq), -18°, 30 min		 (-)	504
		LDA (2.5 eq), THF, 0°	CH <sub>3</sub> I	 (99) <i>anti</i>	508
		LDA (2.5 eq), THF, 0°	CH <sub>3</sub> I	A. B. (59) A: 2, B: 98	508
307		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -60°, 30 min		 (44)	311, 429, 525

TABLE XXXVIII. THIOETHERS (Continued)

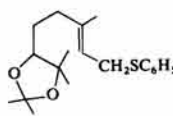
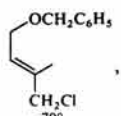
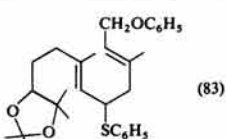
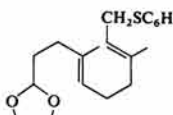
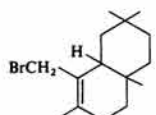
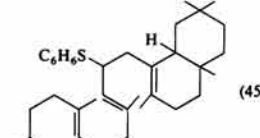
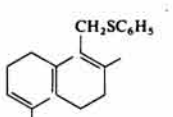
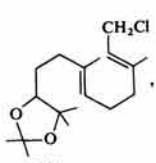
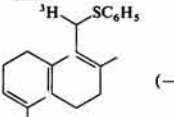
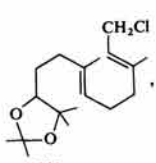
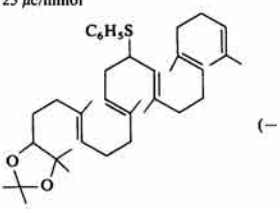
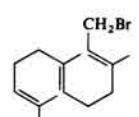
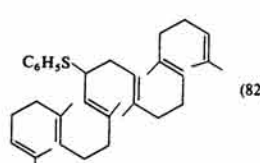
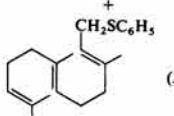
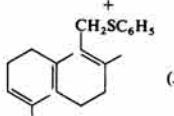
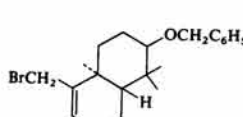
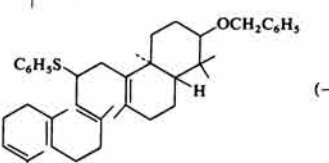
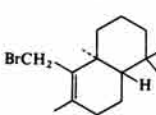
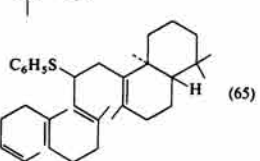
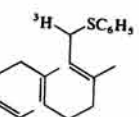
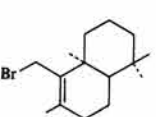
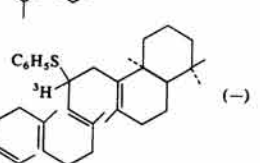
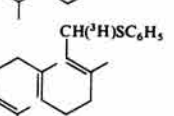
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>19</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -20°, 1 hr		 (83)	320
	C <sub>6</sub> H <sub>5</sub> SCH=C(CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	LDA, THF, 0°, 45 min	CH <sub>2</sub> O, -78°, 15 min	C <sub>6</sub> H <sub>5</sub> SCH=C(CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )CH(CH <sub>2</sub> OH)SC <sub>2</sub> H <sub>5</sub> (84)	584
308 C <sub>20</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF		 (45)	592
C <sub>21</sub>		<i>n</i> -BuLi, DABCO, THF, -18°, <sup>3</sup> H <sub>2</sub> O 30 min		 (-) 25 μc/mmol	87, 629
				 (-)	320
				 (82)	87, 295
				 (3)	
309		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, DABCO, -35°		 (-)	593
				 (65)	593
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF		 (-)	629
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 3:1, 20°	<sup>3</sup> H <sub>2</sub> O	 (-)	226

TABLE XXXVIII. THIOETHERS (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
310 C <sub>21</sub> (Contd.)		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF-[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, 3:1, 20°			226, 592
		CH <sub>3</sub> Li, THF			321
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -18°, 30 min			87, 295
311 C <sub>26</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF	—		478, 628
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, -78°	—		242
311 C <sub>28</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, DABCO, THF, -23°			623
		[(CH <sub>3</sub> ) <sub>2</sub> Si] <sub>2</sub> NK, THF, 1.6 hr, 40°	—		327b
311 C <sub>31</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA, -50°, then 20°, 2 hr	ClCH <sub>2</sub> (CH <sub>3</sub> )C=CHCH <sub>2</sub> OTHP (E)		480

\* Asterisks denote tritium-labeled positions.

TABLE XXXIX. THIOISONITRILES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>4</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> NCS	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -60°, 15 min	C <sub>6</sub> H <sub>5</sub> CHO, 0°, 15 min	 <i>cis</i> : 1, <i>trans</i> : 1 (15)	22
C <sub>8</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NCS	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, THF, -60°, 15 min	C <sub>6</sub> H <sub>5</sub> CHO, 0°, 15 min	 <i>cis</i> : 1, <i>trans</i> : 2 (75)	22

TABLE XL. THIOKETONES

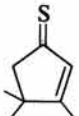
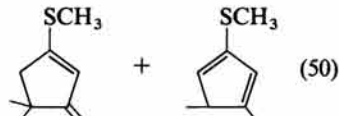
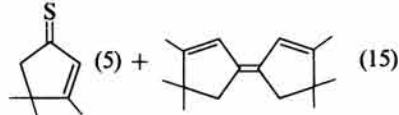
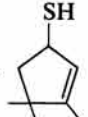
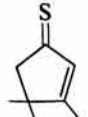
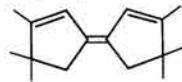
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub>		CH <sub>3</sub> MgBr (2.5 eq), THF, 3 hr	H <sub>2</sub> O		506
					
		C <sub>2</sub> H <sub>5</sub> MgBr (2.5 eq), THF, 3 hr	H <sub>2</sub> O	A,  + B,  + C, 	
	<i>i</i> -C <sub>3</sub> H <sub>7</sub> MgBr (2.5 eq), THF, 3 hr	H <sub>2</sub> O	A (-), B (10), C (60) A (-), B (10), C (60)	506 506	

TABLE XL. THIOKETONES (Continued)

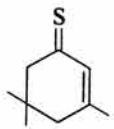
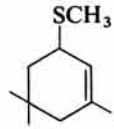
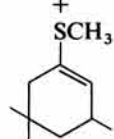
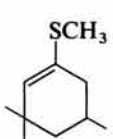
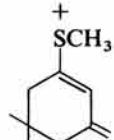
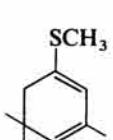
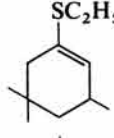
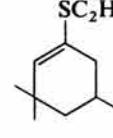
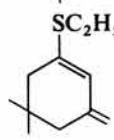
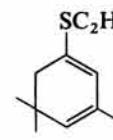
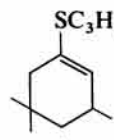
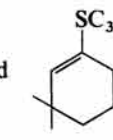
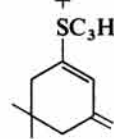
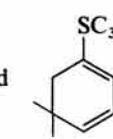
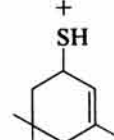
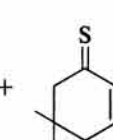
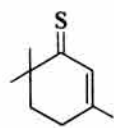
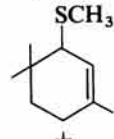
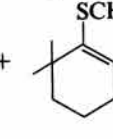
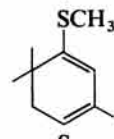
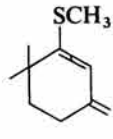
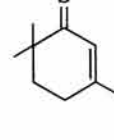
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>9</sub>		CH <sub>3</sub> MgBr (2.5 eq), THF, 3 hr	H <sub>2</sub> O	 (20)	506
				+  and  (20)	
				+  and  (45)	
		C <sub>2</sub> H <sub>5</sub> MgBr (2.5 eq), THF, 3 hr	H <sub>2</sub> O	 and  (20)	506
			+  and  (50)		
		<i>i</i> -C <sub>3</sub> H <sub>7</sub> MgBr (2.5 eq), THF, 3 hr	H <sub>2</sub> O	 and  (10)	506
			+  and  (35)		
				+  (5) +  (40)	
C <sub>9</sub>		CH <sub>3</sub> MgBr (2.5 eq), THF, 3 hr	H <sub>2</sub> O	 (10) +  (30)	506
				+  and  (35)	
				+  (15)	



TABLE XL. THIOKETONES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>9</sub> (Contd.)		C <sub>2</sub> H <sub>5</sub> MgBr (2.5 eq), THF, 3 hr	H <sub>2</sub> O	(10) +  (15) +  (30) and  (30) +  (15)	506
		<i>i</i> -C <sub>3</sub> H <sub>7</sub> MgBr (2.5 eq), THF, 3 hr	H <sub>2</sub> O	(10) +  (15) +  (15) and  (15) +  (15)	506
C <sub>11</sub>	C <sub>6</sub> H <sub>5</sub> CSC <sub>4</sub> H <sub>9</sub> - <i>t</i>	CH <sub>3</sub> MgBr, ether, 16 hr	H <sub>2</sub> O	(5) +  (45)	388
		CH <sub>3</sub> Li, ether, 15 min	H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CH(SCH <sub>3</sub> )C <sub>4</sub> H <sub>9</sub> - <i>t</i> + B, C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )(SH)C <sub>4</sub> H <sub>9</sub> - <i>t</i> + C, C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )(SCH <sub>3</sub> )C <sub>4</sub> H <sub>9</sub> - <i>t</i> A: 57, B: 28, C: 15 (-)	388
		CH <sub>3</sub> MgBr, THF, 15 min	H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CH(SCH <sub>3</sub> )C <sub>4</sub> H <sub>9</sub> - <i>t</i>	388
		<i>n</i> -C <sub>5</sub> H <sub>11</sub> MgBr, THF, 1 hr	H <sub>2</sub> O	B, C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )(SH)C <sub>4</sub> H <sub>9</sub> - <i>t</i> A: 22, B: 78 (-)	388
		<i>n</i> -C <sub>6</sub> H <sub>13</sub> MgBr, THF, 15 hr	H <sub>2</sub> O	C, C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )(SCH <sub>3</sub> )C <sub>4</sub> H <sub>9</sub> - <i>t</i> (10) C <sub>6</sub> H <sub>5</sub> CH(SC <sub>5</sub> H <sub>11</sub> - <i>n</i> )C <sub>4</sub> H <sub>9</sub> - <i>t</i> (-)	388
			H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CH(SC <sub>6</sub> H <sub>13</sub> - <i>n</i> )C <sub>4</sub> H <sub>9</sub> - <i>t</i> + B, C <sub>6</sub> H <sub>5</sub> CH(SH)C <sub>4</sub> H <sub>9</sub> - <i>t</i> A: 40, B: 60 (-)	388
		C <sub>2</sub> H <sub>5</sub> MgBr, ether, 15 min	H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CH(SC <sub>2</sub> H <sub>5</sub> )C <sub>4</sub> H <sub>9</sub> - <i>t</i> + B, C <sub>6</sub> H <sub>5</sub> CH(SH)C <sub>4</sub> H <sub>9</sub> - <i>t</i> + C, C <sub>6</sub> H <sub>5</sub> C(C <sub>2</sub> H <sub>5</sub> )(SC <sub>2</sub> H <sub>5</sub> )C <sub>4</sub> H <sub>9</sub> - <i>t</i> A: 46, B: 54, C: trace (-)	388
C <sub>2</sub> H <sub>5</sub> MgBr, THF, 15 min	H <sub>2</sub> O	A: 37, B: 38, C: 25 (-)	388		
<i>n</i> -C <sub>3</sub> H <sub>7</sub> MgBr, ether, 15 min	H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CH(SC <sub>3</sub> H <sub>7</sub> - <i>n</i> )C <sub>4</sub> H <sub>9</sub> - <i>t</i> + B, C <sub>6</sub> H <sub>5</sub> CH(SH)C <sub>4</sub> H <sub>9</sub> - <i>t</i> A: 5, B: 95 (-)	388		

TABLE XL. THIOKETONES (Continued)



No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>11</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CSC <sub>4</sub> H <sub>9</sub> - <i>t</i>	<i>n</i> -C <sub>3</sub> H <sub>7</sub> MgBr, THF, 15 min	H <sub>2</sub> O	A: 50, B: 50 (—)	388
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> MgBr, ether, 15 min	H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CH(SC <sub>4</sub> H <sub>9</sub> - <i>n</i> )C <sub>4</sub> H <sub>9</sub> - <i>t</i> + B, C <sub>6</sub> H <sub>5</sub> CH(SH)C <sub>4</sub> H <sub>9</sub> - <i>t</i>	
C <sub>13</sub>	C <sub>6</sub> H <sub>5</sub> CSC <sub>6</sub> H <sub>5</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> MgBr, THF, 15 min	H <sub>2</sub> O	A: trace, B: 100 (—)	388
		CH <sub>3</sub> MgBr (10 eq), THF, -70°	H <sub>2</sub> O	A: 67, B: 33 A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(CH <sub>3</sub> )SCH <sub>3</sub> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CH <sub>2</sub>	
		20 min	H <sub>2</sub> O	A: 65, B: 35 (—)	389
		2 hr	H <sub>2</sub> O	A: 100, B: 0 (—)	
		CH <sub>3</sub> MgI (5 eq), ether, 16 hr	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CC(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>   S + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (95, total)	389
		CH <sub>3</sub> Li (5 eq), ether, 16 hr	H <sub>2</sub> O	A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSCH <sub>3</sub> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CH <sub>2</sub>	
		C <sub>2</sub> H <sub>5</sub> MgBr (5 eq), ether, 16 hr	H <sub>2</sub> O	A: 30, B: 70 (—) A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>2</sub> H <sub>5</sub> + B, C <sub>6</sub> H <sub>5</sub> CSC <sub>6</sub> H <sub>5</sub>	389
		C <sub>2</sub> H <sub>5</sub> MgBr (5 eq), THF, 20 min	H <sub>2</sub> O	A: 67, B: 29 (—) A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>2</sub> H <sub>5</sub> (90) + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHCH <sub>3</sub> (5)	
		<i>i</i> -C <sub>3</sub> H <sub>7</sub> MgBr (5 eq), THF, 20 min	H <sub>2</sub> O	A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>3</sub> H <sub>7</sub> - <i>i</i> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub> + C, C <sub>6</sub> H <sub>5</sub> CSC <sub>6</sub> H <sub>5</sub>	161, 389
		<i>n</i> -C <sub>3</sub> H <sub>7</sub> MgBr (5 eq), THF, 20 min	H <sub>2</sub> O	A: 63, B: 25, C: 12 (—) A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>3</sub> H <sub>7</sub> - <i>n</i> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHC <sub>2</sub> H <sub>5</sub>	
<i>t</i> -C <sub>4</sub> H <sub>9</sub> MgBr (5 eq), THF, 20 min	H <sub>2</sub> O	A: 88, B: 9 (—) A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>4</sub> H <sub>9</sub> - <i>t</i> (48)	389		
<i>n</i> -C <sub>4</sub> H <sub>9</sub> MgBr (5 eq), THF, 20 min	H <sub>2</sub> O	A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>4</sub> H <sub>9</sub> - <i>n</i> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHC <sub>3</sub> H <sub>7</sub> - <i>n</i>			
<i>t</i> -C <sub>4</sub> H <sub>9</sub> CH <sub>2</sub> MgBr (5 eq), THF, 20 min	H <sub>2</sub> O	A: 20, B: 80 (—) A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSCH <sub>2</sub> C <sub>4</sub> H <sub>9</sub> - <i>t</i> + B, C <sub>6</sub> H <sub>5</sub> CSC <sub>6</sub> H <sub>5</sub>	389		
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CHMgBr (5 eq), THF, 20 min	H <sub>2</sub> O	A: 25, B: 60 (—) A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSCH(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=C(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> + C, C <sub>6</sub> H <sub>5</sub> CSC <sub>6</sub> H <sub>5</sub>			
		 MgBr (5 eq), THF, 20 min	H <sub>2</sub> O	A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSCH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (21)	161, 389
		 MgBr (5 eq), THF, 20 min	H <sub>2</sub> O	A, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSCH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (14)	389

TABLE XL. THIOKETONES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>13</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CSC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> MgBr (5 eq), THF, 20 min	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>6</sub> H <sub>5</sub> (25)	389
		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> MgBr (5 eq), THF, 20 min	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (73)	389
		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cd (2 eq), THF, 1 hr	H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CSC <sub>6</sub> H <sub>5</sub> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>2</sub> H <sub>5</sub> + C, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHCH <sub>3</sub> + D, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> + E, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CC(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>   S	389
		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cd (2 eq), ether, 30 min	H <sub>2</sub> O	A: 50, B: 30, C: 11, D: 3, E: 6 (—) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CC(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (90)   S	389
		( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> Cd (2 eq), THF, 30 min	H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CSC <sub>6</sub> H <sub>5</sub> + B, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>3</sub> H <sub>7-<i>n</i></sub> + C, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> A: 43, B: 20, C: 37 (—)	389
		( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> Cd (2 eq), ether, 30 min	H <sub>2</sub> O	A, C <sub>6</sub> H <sub>5</sub> CSC <sub>6</sub> H <sub>5</sub> + B, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> A: 37, B: 63 (—)	389
		C <sub>6</sub> H <sub>5</sub> MgBr, THF or ether or C <sub>6</sub> H <sub>6</sub>	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>6</sub> H <sub>5</sub> (37-10)	56, 161, 162
		C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>3</sub> MgBr, THF	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHS(CH <sub>2</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>5</sub> (29)	161
		CH <sub>3</sub> MgBr, THF	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSCH <sub>3</sub> (73)	161
		C <sub>2</sub> H <sub>5</sub> MgBr, THF	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>2</sub> H <sub>5</sub> (95)	161
		<i>n</i> -C <sub>3</sub> H <sub>7</sub> MgBr, THF	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>3</sub> H <sub>7-<i>n</i></sub> (79)	161
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> MgBr, THF	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>4</sub> H <sub>9-<i>n</i></sub> (49)	161
		<i>i</i> -C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> CH <sub>2</sub> MgBr, THF	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSCH <sub>2</sub> CH <sub>2</sub> C <sub>3</sub> H <sub>7-<i>i</i></sub> (48)	161
		C <sub>6</sub> H <sub>5</sub> Li, ether, C <sub>6</sub> H <sub>6</sub> , room temperature	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>6</sub> H <sub>5</sub> (70)	162
		C <sub>6</sub> H <sub>5</sub> Li, THF, -70° to 25°	H <sub>2</sub> O CH <sub>3</sub> OD	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>6</sub> H <sub>5</sub> (30-40) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CDSC <sub>6</sub> H <sub>5</sub> (84)	56 56
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>4</sub> H <sub>9-<i>n</i></sub> (25)	56		
C <sub>6</sub> H <sub>5</sub> Na, C <sub>6</sub> H <sub>6</sub>	H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSC <sub>6</sub> H <sub>5</sub> (25)	162		
C <sub>6</sub> H <sub>5</sub> Li, ether	CH <sub>3</sub> OD	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CDSC <sub>6</sub> H <sub>5</sub> (0.88 D) (31)	162		
C <sub>15</sub>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CS	C <sub>6</sub> H <sub>5</sub> Li, THF	(CH <sub>3</sub> ) <sub>3</sub> SiCl	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(SC <sub>6</sub> H <sub>5</sub> )Si(CH <sub>3</sub> ) <sub>3</sub> (37)	162
		C <sub>6</sub> H <sub>5</sub> Li, ether	H <sub>2</sub> O	(C <sub>6</sub> D <sub>5</sub> ) <sub>2</sub> CHSC <sub>6</sub> H <sub>5</sub> (—)	56
		C <sub>6</sub> H <sub>5</sub> Li, ether, C <sub>6</sub> H <sub>6</sub> , room temperature	H <sub>2</sub> O	(C <sub>6</sub> D <sub>5</sub> ) <sub>2</sub> CHSC <sub>6</sub> H <sub>5</sub> (24)	162
		C <sub>6</sub> H <sub>5</sub> Li, ether, C <sub>6</sub> H <sub>6</sub> , room temperature	H <sub>2</sub> O	( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CHSC <sub>6</sub> H <sub>5</sub> (70)	162

TABLE XL. THIOKETONES (Continued)

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>15</sub> (Contd.)	( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CS	C <sub>2</sub> H <sub>5</sub> MgBr, THF, 10 min	H <sub>2</sub> O	A, <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CSC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> + B, C <sub>2</sub> H <sub>5</sub> SCH[C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> ] <sub>2</sub> + C, CH <sub>3</sub> CH=C(C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> - <i>p</i> ) <sub>2</sub> + D, [ <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ] <sub>2</sub> CH <sub>2</sub> A: 3, B: 30, C: 20, D: 15 (—)	389
322 C <sub>17</sub>	[ <i>m,p</i> -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sub>2</sub> CS	C <sub>2</sub> H <sub>5</sub> MgBr, ether, 30 min	H <sub>2</sub> O	A: 56, B: 29, C: 7, D: 0 (—)	389
		C <sub>2</sub> H <sub>5</sub> MgBr, THF, 15 min	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> SCH[C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> - <i>m,p</i> ] <sub>2</sub> (94)	389
		<i>i</i> -C <sub>3</sub> H <sub>7</sub> MgBr, THF, 15 min	H <sub>2</sub> O	A, <i>m,p</i> -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CSC <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> - <i>m,p</i> + B, <i>i</i> -C <sub>3</sub> H <sub>7</sub> SCH[C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> - <i>m,p</i> ] <sub>2</sub> + C, [ <i>m,p</i> -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub> + D, [ <i>m,p</i> -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sub>2</sub> CH <sub>2</sub> A: 5, B: 78, C: 7, D: 10 (—)	389
		<i>n</i> -C <sub>3</sub> H <sub>7</sub> MgBr, ether, 15 min	H <sub>2</sub> O	A, <i>m,p</i> -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CSC <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> - <i>m,p</i> + B, <i>n</i> -C <sub>3</sub> H <sub>7</sub> SCH[C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> - <i>m,p</i> ] <sub>2</sub> + C, [ <i>m,p</i> -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sub>2</sub> CH <sub>2</sub> A: 56, B: 18, C: 21 (—)	389
	[ <i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ] <sub>2</sub> CS	C <sub>6</sub> H <sub>5</sub> Li, THF	H <sub>2</sub> O	[ <i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ] <sub>2</sub> CHSC <sub>6</sub> H <sub>5</sub> (60–70)	162

TABLE XLI. THIOLS

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>3</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> SH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), TMEDA, <i>n</i> -C <sub>6</sub> H <sub>14</sub> , 0°, 3 hr	CH <sub>2</sub> =CHCH <sub>2</sub> Br, -78°, THF	A, RCH <sub>2</sub> CH=CHSR' +	
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.1 eq), THF, TMEDA (1-2 eq), 0°, 4 hr	C <sub>2</sub> H <sub>5</sub> Br (2.1 eq) <i>i</i> -C <sub>3</sub> H <sub>7</sub> Cl (1.1 eq), then C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (1.1 eq) [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (30%), <i>i</i> -C <sub>3</sub> H <sub>7</sub> Cl (1 eq), then C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (1 eq) <i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (12%), <i>i</i> -C <sub>3</sub> H <sub>7</sub> Cl (1 eq), then C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (1 eq) <i>n</i> -C <sub>5</sub> H <sub>11</sub> Cl (1.1 eq), then CH <sub>3</sub> I (1.1 eq) <i>n</i> -C <sub>6</sub> H <sub>13</sub> Br (1.1 eq), then CH <sub>3</sub> I (1.1 eq) <i>n</i> -C <sub>8</sub> H <sub>17</sub> Cl (1.1 eq), then CH <sub>3</sub> I (1.1 eq) <i>n</i> -C <sub>8</sub> H <sub>17</sub> Cl (2 eq)	B, CH <sub>2</sub> =CHCHRSR' A: 25, B: 9, R = R' = CH <sub>2</sub> CH=CH <sub>2</sub> A: 77, B: 23, R = R' = C <sub>2</sub> H <sub>5</sub> (65) A: 68, B: 32, R = C <sub>3</sub> H <sub>7</sub> - <i>i</i> , R' = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (80) A: 22, B: 78, R' = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> , R = <i>i</i> -C <sub>3</sub> H <sub>7</sub> (82) A: 35, B: 65, R' = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> , R = <i>i</i> -C <sub>3</sub> H <sub>7</sub> (50) A: 76, B: 24, R = C <sub>5</sub> H <sub>11</sub> - <i>n</i> , R' = CH <sub>3</sub> (77) A: 78, B: 22, R = C <sub>6</sub> H <sub>13</sub> - <i>n</i> , R' = CH <sub>3</sub> (90) A: 74, B: 26, R = C <sub>8</sub> H <sub>17</sub> - <i>n</i> , R' = CH <sub>3</sub> (87) A: 73, B: 27, R = R' = C <sub>8</sub> H <sub>17</sub> - <i>n</i> (81)	89 43 43, 630 630 43 43, 630 43, 630 630

TABLE XLI. THIOLS (Continued)

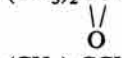
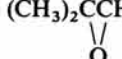
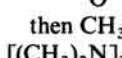
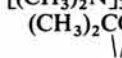
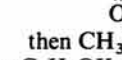
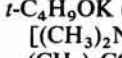
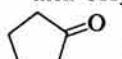

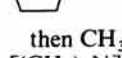
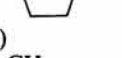
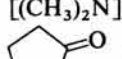
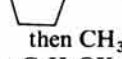

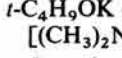
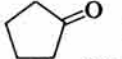
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>3</sub> (Contd.)	CH <sub>2</sub> =CHCH <sub>2</sub> SH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.1 eq), THF, TMEDA (1-2 eq), 0°, 4 hr	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (30%), <i>n</i> -C <sub>8</sub> H <sub>17</sub> Cl (2 eq) <i>n</i> -C <sub>10</sub> H <sub>21</sub> Br (2.1 eq)	A: 88, B: 12, R = R' = C <sub>8</sub> H <sub>17-n</sub> (80)	630
			C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (2.1 eq)	A: 77, B: 23, R = R' = C <sub>10</sub> H <sub>21-n</sub> (90)	43
			(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> (2.1 eq)	A: 73, B: 27, R = R' = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (67)	43
			 (1 eq), then CH <sub>3</sub> I (1 eq)	A: 78, B: 22, R = R' = CH <sub>2</sub> C(OH)(CH <sub>3</sub> ) <sub>2</sub> (86)	43
			 (1 eq), then CH <sub>3</sub> I (1 eq)	A: 64, B: 36 R' = CH <sub>3</sub> , R = CH <sub>2</sub> C(OH)(CH <sub>3</sub> ) <sub>2</sub> (60)	630
			 (1 eq), then CH <sub>3</sub> I (1 eq)	A: 76, B: 24 R' = CH <sub>3</sub> , R = CH <sub>2</sub> C(OH)(CH <sub>3</sub> ) <sub>2</sub> (45)	630
			 (1 eq), then CH <sub>3</sub> I (1 eq)	A: 86, B: 14 R' = CH <sub>3</sub> , R = CH <sub>2</sub> C(OH)(CH <sub>3</sub> ) <sub>2</sub> (60)	630
			 (1 eq), then CH <sub>3</sub> I (1 eq)	A: 76, B: 24, R = Si(CH <sub>3</sub> ) <sub>3</sub> , R' = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (76-89)	43, 630
			 (1 eq), then CH <sub>3</sub> I (1.1 eq), then C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (1.1 eq)		
			[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (30%) added	A: 82, B: 18 R' = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> , R = (CH <sub>3</sub> ) <sub>3</sub> Si (80)	630
			CH <sub>3</sub> OH (1 eq), then C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	A: 84, B: 16, R' = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> , R = H (90)	630
			[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (30%) added	A: 81, B: 19, R' = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> , R = H (86)	630
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq), then [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (12%) added	A: 92, B: 8, R' = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> , R = H (85)	630
			C <sub>2</sub> H <sub>5</sub> CHO (1.1 eq), then CH <sub>3</sub> I (1.1 eq)	A: 74, B: 26, R = CH(OH)C <sub>2</sub> H <sub>5</sub> , R' = CH <sub>3</sub> (69)	43
			C <sub>6</sub> H <sub>5</sub> CHO (1.1 eq), then CH <sub>3</sub> I (1.1 eq)	A: 67, B: 33, R = CH(OH)C <sub>6</sub> H <sub>5</sub> , R' = CH <sub>3</sub> (89)	43
			 (1.1 eq), then CH <sub>3</sub> I (1.1 eq)	A: 72, B: 28, R =  , R' = CH <sub>3</sub> (73)	43, 630
			 (1 eq), then CH <sub>3</sub> I (1.1 eq)	A: 52, B: 48, R' = CH <sub>3</sub> , R =  , R' = CH <sub>3</sub> (80)	630
			 (1 eq), then CH <sub>3</sub> I (1 eq)	A: 80, B: 20,	630
 (1 eq), then CH <sub>3</sub> I (1 eq)	R =  , R' = CH <sub>3</sub> (35)				
 (1.1 eq), then CH <sub>3</sub> I (1.1 eq)	A: 70, B: 30, R = C(OH)(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> ), R' = CH <sub>3</sub> (95)	43			
 (1.1 eq), then CH <sub>3</sub> I (1.1 eq)	A: 75, B: 25, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> , R' = CH <sub>3</sub> (88)	43, 630			

TABLE XLI. THIOLS (Continued)

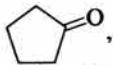

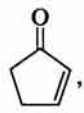
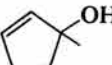
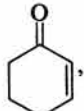
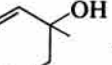

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.	
C <sub>3</sub> (Contd.)	CH <sub>2</sub> =CHCH <sub>2</sub> SH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.1 eq), THF, TMEDA (1-2 eq), 0°, 4 hr	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (12%), C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (1 eq), then CH <sub>3</sub> I (1 eq)	A: 90, B: 10, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> , R' = CH <sub>3</sub> (76)	630	
			CH <sub>3</sub> SSCH <sub>3</sub> (1.1 eq), then CH <sub>3</sub> I (1.1 eq)	A: 80, B: 20, R = SCH <sub>3</sub> , R' = CH <sub>3</sub> (70)	43	
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, ether, MgBr <sub>2</sub> (1 eq), ether	C <sub>2</sub> H <sub>5</sub> CHO, then CH <sub>3</sub> I	CH <sub>2</sub> =CHCHRSR'	267
				A, R = CH(OH)C <sub>2</sub> H <sub>5</sub> , R' = CH <sub>3</sub> (91)	267	
				<i>i</i> -C <sub>3</sub> H <sub>7</sub> CHO, then CH <sub>3</sub> I	A, R = CH(OH)C <sub>3</sub> H <sub>7</sub> - <i>i</i> , R' = CH <sub>3</sub> (98)	267
				C <sub>6</sub> H <sub>5</sub> CHO, then CH <sub>3</sub> I	A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> , R' = CH <sub>3</sub> (73)	267
				 then CH <sub>3</sub> I	A, R =  , R' = CH <sub>3</sub> (94)	267
				C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> , then CH <sub>3</sub> I	A, R = C(OH)(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> , R' = CH <sub>3</sub> (89)	267
				CH <sub>2</sub> =CHCOCH <sub>3</sub> , then CH <sub>3</sub> I	A, R = C(OH)(CH <sub>3</sub> )CH=CH <sub>2</sub> , R' = CH <sub>3</sub> (84)	267
				CH <sub>3</sub> CH=CHCOCH <sub>3</sub> , then CH <sub>3</sub> I	A, R = C(OH)(CH <sub>3</sub> )CH=CHCH <sub>3</sub> , R' = CH <sub>3</sub> (95)	267
				(CH <sub>3</sub> ) <sub>2</sub> C=CHCOCH <sub>3</sub> , then CH <sub>3</sub> I	A, R = C(OH)CH=C(CH <sub>3</sub> ) <sub>2</sub> , R' = CH <sub>3</sub> (95)	267
				 then CH <sub>3</sub> I	A, R =  , R' = CH <sub>3</sub> (90)	267
				 then CH <sub>3</sub> I	A, R =  , R' = CH <sub>3</sub> (91)	267, 630
			C <sub>4</sub>	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, TMEDA (2 eq), -80°	<i>n</i> -C <sub>8</sub> H <sub>17</sub> Cl (1 eq), then CH <sub>3</sub> I (1 eq)
<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq), [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO (15%), <i>n</i> -C <sub>8</sub> H <sub>17</sub> Cl (1 eq), then CH <sub>3</sub> I (1 eq)	A: 69, B: 31, R = C <sub>8</sub> H <sub>17</sub> - <i>n</i> , R' = CH <sub>3</sub> (68)	630				
C <sub>2</sub> H <sub>5</sub> CHO (1 eq), then CH <sub>3</sub> I	A: 54, B: 46, R = C <sub>2</sub> H <sub>5</sub> CH(OH), R' = CH <sub>3</sub> (80)	630				
	A: 66, B: 34, R =  , R' = CH <sub>3</sub> (80)	630				
	A: 49, B: 51, R = C <sub>6</sub> H <sub>5</sub> CH(OH), R' = CH <sub>3</sub> (95)	630				
	A: 73, B: 27, R = C <sub>6</sub> H <sub>5</sub> CH(OH), R' = CH <sub>3</sub> (80)	630				

TABLE XLI. THIOLS (Continued)

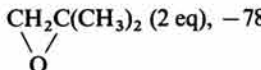
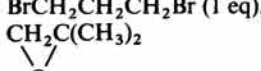
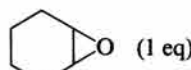
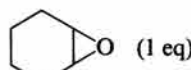
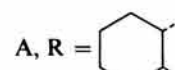
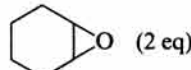
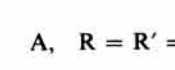
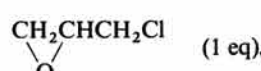
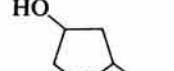
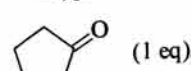
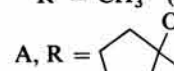
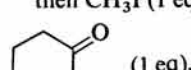
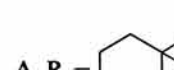
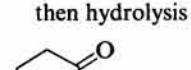
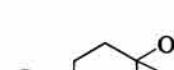
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>4</sub> (Contd.)	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> SH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2 eq), THF, TMEDA (2 eq), -80°	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (1 eq), then CH <sub>3</sub> I (1 eq)	A: 61, B: 39, R = (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH), R' = CH <sub>3</sub> (90)	630
			<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK (1 eq), 30% [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO, C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (1 eq), then CH <sub>3</sub> I (1 eq)	A: 82, B: 18, R = (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH), R' = CH <sub>3</sub> (75)	630
C <sub>7</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SH	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OK, (CH <sub>3</sub> ) <sub>2</sub> NCHO, 80° <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF- <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 1:1, 50°, 4 hr or <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF- <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 1:1, -5°, 2.5 hr	—	C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (0.5)	599
			CH <sub>3</sub> I (2 eq), -78°	C <sub>6</sub> H <sub>5</sub> CHRSR' A, R = R' = CH <sub>3</sub> (72)	118, 630
			 (2 eq), -78°	A, R = R' = CH <sub>2</sub> C(OH)C(CH <sub>3</sub> ) <sub>2</sub> (70)	118, 630
			BrCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br (1 eq), -78°	A, R = R' = (CH <sub>2</sub> ) <sub>3</sub> (67)	118, 630
			 (1 eq), then CH <sub>2</sub> =CHCH <sub>2</sub> Br (1 eq)	A, R = (CH <sub>3</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> (70)	630
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> I (1 eq), then CH <sub>3</sub> I (1 eq)	R' = CH <sub>2</sub> =CHCH <sub>2</sub> (63)	630
			CH <sub>2</sub> =CHCH <sub>2</sub> Br (1 eq), then CH <sub>3</sub> I	A, R = C <sub>4</sub> H <sub>9</sub> - <i>n</i> , R' = CH <sub>3</sub> (75)	630
			<i>n</i> -C <sub>7</sub> H <sub>15</sub> I (2 eq)	A, R = CH <sub>2</sub> =CHCH <sub>2</sub> , R' = CH <sub>3</sub> (55)	630
			 (1 eq), then CH <sub>3</sub> I, -78°	A, R = R' = C <sub>7</sub> H <sub>15</sub> - <i>n</i> (60)	630
			 (1 eq), then CH <sub>3</sub> I, -78°	A, R =  , R' = CH <sub>3</sub> (76)	118
			 (2 eq), -78°	A, R = R' =  (80)	118
			 (1 eq), -78°	HO-  (44)	118, 630
			<i>n</i> -C <sub>4</sub> H <sub>9</sub> CHO (1 eq), then CH <sub>3</sub> I (1 eq), -78°	C <sub>6</sub> H <sub>5</sub> CHRSR' A, R = CH(OH)C <sub>4</sub> H <sub>9</sub> - <i>n</i> , R' = CH <sub>3</sub> (90)	118, 630
C <sub>6</sub> H <sub>5</sub> CHO (1 eq), -78°	A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> , R' = H (70)	118, 630			
C <sub>6</sub> H <sub>5</sub> CHO (1 eq), then CH <sub>3</sub> I (1 eq), -78°	A, R = CH(OH)C <sub>6</sub> H <sub>5</sub> , R' = CH <sub>3</sub> (82)	118, 630			
 (1 eq), then CH <sub>3</sub> I (1 eq)	A, R =  , R' = CH <sub>3</sub> (72)	630			
 (1 eq), then hydrolysis	A, R =  , R' = H (65)	630			
 (1 eq), then CH <sub>3</sub> I (1 eq)	A, R =  , R' = CH <sub>3</sub> (85)	630			



TABLE XLI. THIOLS (Continued)

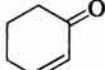
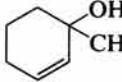
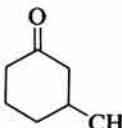


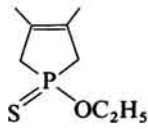
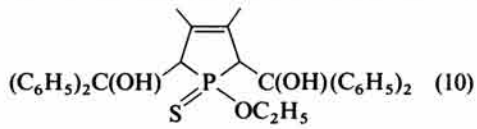
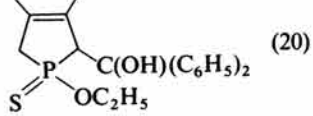
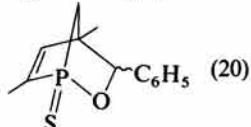
No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>7</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF- <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 1:1, 50°, 4 hr or <i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, TMEDA, THF- <i>n</i> -C <sub>5</sub> H <sub>12</sub> , 1:1, -5°, 2.5 hr	 (1 eq), then CH <sub>3</sub> I (1 eq), -78°	 (61) +  (14)	118, 630
			 (1 eq), then CH <sub>3</sub> I (1 eq), -78° C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (1 eq), then CH <sub>3</sub> I (1 eq)	 (34) + C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SCH <sub>3</sub> (45) C <sub>6</sub> H <sub>5</sub> CHRSR'	118, 630
			(CH <sub>3</sub> ) <sub>3</sub> SiCl (1 eq), -78° (CH <sub>3</sub> ) <sub>3</sub> SiCl (2 eq), -78° (CH <sub>3</sub> ) <sub>3</sub> SiCl (1 eq), then CH <sub>3</sub> I (1 eq), -78°	A, R = C(OH)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> , R' = CH <sub>3</sub> (48)	118
			(CH <sub>3</sub> ) <sub>3</sub> SiCl (1 eq), -78° (CH <sub>3</sub> ) <sub>3</sub> SiCl (2 eq), -78°	A, R = Si(CH <sub>3</sub> ) <sub>3</sub> , R' = H (73)	118, 630
			(CH <sub>3</sub> ) <sub>3</sub> SiCl (1 eq), then CH <sub>3</sub> I (1 eq), -78° CH <sub>3</sub> SSCH <sub>3</sub> (1 eq), then C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br (1 eq), -78°	A, R = Si(CH <sub>3</sub> ) <sub>3</sub> , R' = CH <sub>3</sub> (62-91) A, R = SCH <sub>3</sub> , R' = CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (73)	118, 630

TABLE XLII. THIOPHOSPHINATES

No. of C Atoms	Reactant	Base and Conditions	Quenching Reagent	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub>		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li (2.2 eq), THF, -75°	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub> (2.5 eq)	 (10)	39
		<i>n</i> -C <sub>4</sub> H <sub>9</sub> Li, THF, TMEDA, -75°	C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	 (20)	39
			C <sub>6</sub> H <sub>5</sub> CHO	 (20)	39

**End** The content of *n*-butyllithium can be determined by several methods. (95-98) Lithium salts are present in some commercial preparations.

**Notes**

\*

\* *Ortho* metalation of methyl toluenesulfonate has been found with methyllithium. (231)

\* For drying tetrahydrofuran, see *Org. Synth.*, **46**, 105 (1966).

\* In most of the preparations lithium diisopropylamide is prepared first and the product to be metalated is then added.

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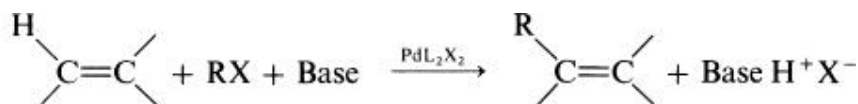
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# Palladium-Catalyzed Vinylation of Organic Halides

Richard F. Heck, University of Delaware, Newark, Delaware

## 1. Introduction

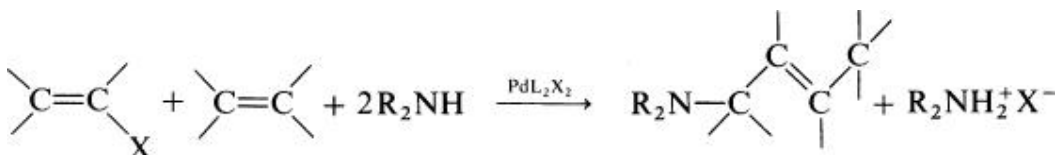
The palladium-catalyzed vinylation of organic halides provides a very convenient method for forming carbon-carbon bonds at unsubstituted vinylic positions. Generally the reaction does not require anhydrous or anaerobic conditions although it is advisable to limit access of oxygen when arylphosphines are used as a component of the catalyst. The transformation is valuable because it cannot be carried out in a single step by any other known method (except in certain Meerwein reactions). The general reaction is



R = Aryl, heterocyclic, benzyl, or vinylic  
X = Bromide, iodide, or (rarely) chloride  
L = A ligand

The organic halide employed is limited to aryl, heterocyclic, benzyl, or vinylic types, with bromides and iodides seen most often. Halides with an easily eliminated beta-hydrogen atom (*i.e.*, alkyl derivatives) cannot be used since they form only olefins by elimination under the normal reaction conditions. The base needed may be a secondary or tertiary amine, sodium or potassium acetate, carbonate, or bicarbonate.

When nucleophilic secondary amines are used as coreactants with most vinylic halides, a variation occurs that often produces tertiary allylic amines as major products.



The catalyst is commonly palladium acetate, although palladium chloride or preformed triarylphosphine palladium complexes, as well as palladium on charcoal, have been used. A reactant, product, or solvent may serve as the ligand L in reactions involving organic iodides, but generally a triarylphosphine

or a secondary amine is required when organic bromides are used. The reaction, which occurs between ca. 50° and 160°, proceeds homogeneously. Solvents such as acetonitrile, dimethylformamide, hexamethylphosphoramide, N-methylpyrrolidinone, and methanol have been used, but are often not necessary. The procedure is applicable to a very wide range of reactants and yields are generally good to excellent.

Several variations of the reaction are known in which the organic halide is replaced by other reagents such as organometallics, diazonium salts, or aromatic hydrocarbons. These reactions are not discussed in detail, but are only briefly compared with the halide reaction. Other related reactions such as the palladium-catalyzed replacement of allylic substituents with carbanionic reagents, (1) the palladium-promoted nucleophilic substitutions at olefinic carbons, (2, 3) and the numerous palladium-catalyzed coupling reactions of halides and organometallics (4) are also beyond the scope of this review. The palladium-catalyzed vinylic substitution reaction has not yet received much attention from organic chemists, but its broad scope and simplicity demonstrate that it is a useful method for the synthesis of a variety of olefinic compounds.

## 2. Mechanism

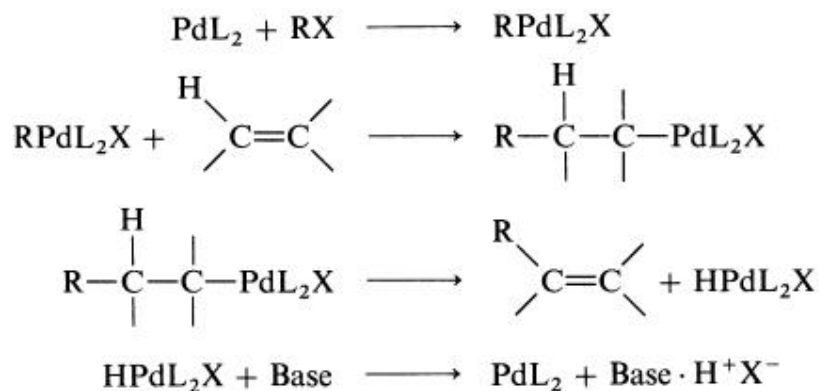
The detailed mechanism of the reaction has not been established, but a fairly accurate approximation can be made based on the products obtained and the large amount of information available from related studies with other organopalladium reactions.

Stoichiometric reactions with organopalladium compounds indicate that they are involved in the vinylic substitution. (5, 6) If a palladium(II) complex or salt is the catalyst introduced, then it must be reduced under the reaction conditions, presumably by oxidizing some of the olefin present. (7) The palladium(0) complex or finely divided metal so formed then reacts with the organic halide to form the organopalladium halide intermediate. This species generally is solvated or coordinated with a pair of two-electron-donating ligands. The organopalladium complex then adds to the double bond of the olefin. The resulting adduct is believed to undergo elimination of a hydridopalladium halide if an  $sp^3$ -bonded hydrogen atom is present beta to the palladium group. The reaction is catalyzed by palladium in the presence of a base because the hydridopalladium halide dissociates reversibly and the base shifts the equilibrium to the palladium(0) species. This latter compound rereacts with the organic halide and the cycle begins again.

Catalyst formation:



Catalytic cycle:

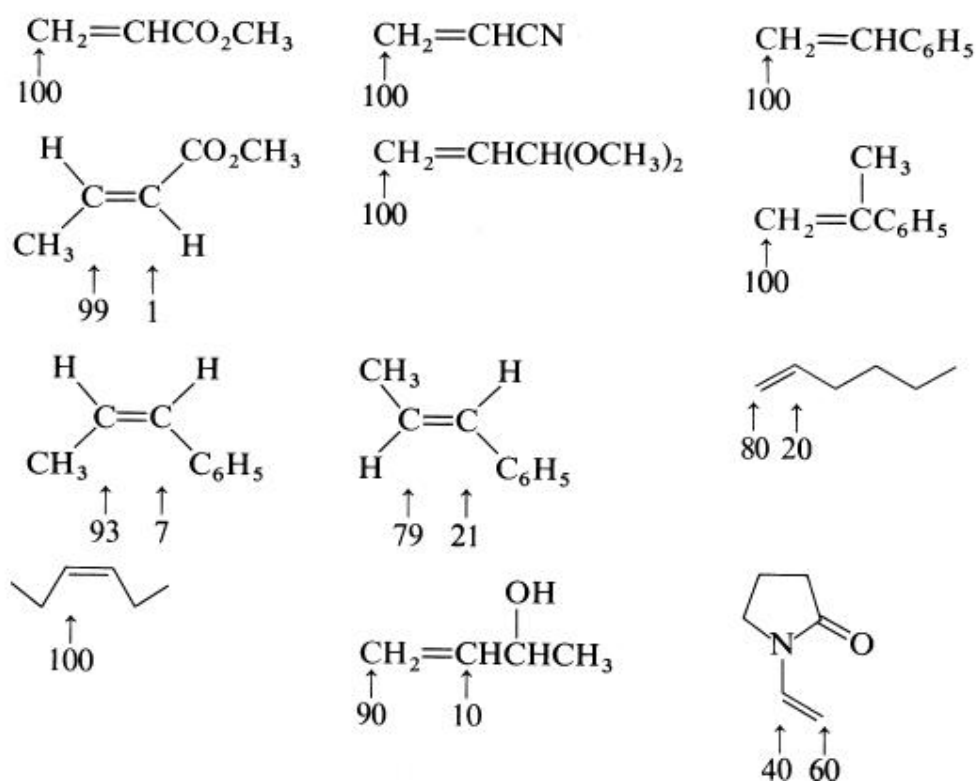


The direction of addition of the organopalladium species to unsymmetrically



substituted double bonds appears to be largely sterically controlled. The organic group behaves as the larger part of the palladium complex, and it goes on the less substituted carbon atom of the double bond. (6) If an electron-withdrawing group is attached to one carbon atom of the double bond, however, addition of the organic group generally takes place exclusively or, at least, predominantly on the other carbon atom. The presence of an electron-donating substituent often causes mixtures of products to be formed with the sterically favored isomer predominating. For example, bromo- or iodobenzene reacts with a variety of olefins, giving products with the percentages of phenyl addition to the olefinic carbons shown below. (8) With

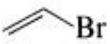
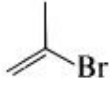

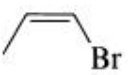
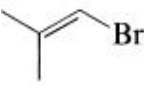
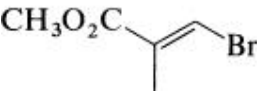
### Orientation of Addition of Bromo- or Iodobenzene to Various Olefins



halides other than bromo- or iodobenzene the orientations are somewhat different. Similar electronic effects are noted when electron-donating or -withdrawing substituents are present in effective positions in the organic halide reactants. (8) For example, *p*-bromodimethylaniline gives more (33%) (9) 2-arylated product with 1-hexene than does bromobenzene (20%). (4)

A series of vinylic bromides have been reacted with 1-hexene and with piperidine or morpholine as the base. (10) Vinyl bromide and 2-bromopropene add exclusively terminally, but  $\beta$ -substituted vinylic bromides give mixtures.

The ratios of terminal to internal (2-position) addition of the organic groups to 1-hexene are as follows: (8, 10)

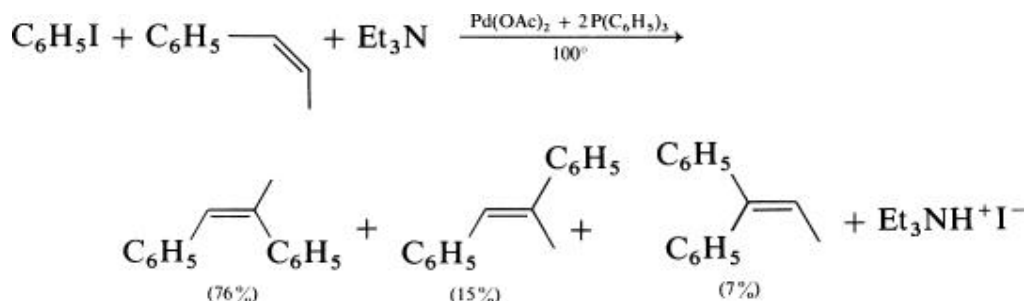
Organic Bromide	Ratio of Terminal to Internal Addition to 1-Hexene
	> 20
	> 20
	1.8
	1.8
	1.7
	4.6

As in the bromo- or iodobenzene reactions shown above, the ratios of products obtained in the vinylic halide reactions are very dependent on the substituents on the double-bond carbons. For instance, all vinylic bromides listed above add exclusively terminally to methyl acrylate (11) and acrolein dimethyl acetal, (12a) whereas mixtures are obtained with all of the halides in the reaction with allyl alcohol. (12b)

A complication in the reaction may appear if there is more than one  $sp^3$ -bonded hydrogen atom beta to the palladium group in the olefin adduct. A mixture of geometric isomers may result or the double bond may be moved from its original position.

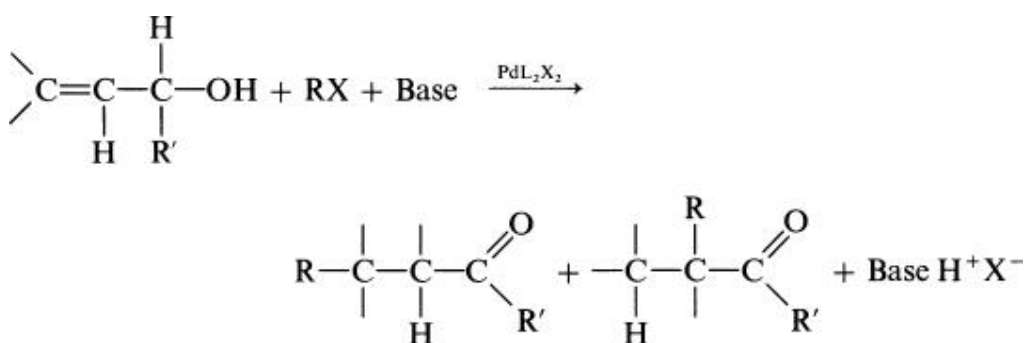
The addition of the organopalladium halide occurs in a *syn* manner and the elimination of the hydridopalladium halide also is *syn*. The stereospecificity of the reaction depends on the reaction conditions. The lower the reaction temperature, the higher are the stereo- and regioselectivity. (6) More important is the influence of triarylphosphines. Iodobenzene and *cis*-1-phenyl-1-propene with triethylamine and palladium acetate as the catalyst at 100° produce only 13.5% *cis*-1,2-diphenyl-1-propene, the stereospecific product, and 57% of the *trans* isomer. The same reaction with two equivalents of triphenylphosphine added per palladium acetate gives 76% of the *cis* isomer and only 15% of the *trans* product. The presence of the phosphine does not affect the direction of addition of the phenylpalladium halide since about the same amount,  $6 \pm 1\%$ ,

of 1,1-diphenyl-1-propene is obtained in both reactions. The triphenylphosphine is believed to decrease the



rate of readdition of the hydridopalladium group in an olefin  $\pi$ -complex intermediate to the double bond, relative to its rate of dissociation from the complex. Since the isomerization occurs by the reverse readdition to and reelimination of the metal hydride from the intermediate, the phosphine improves the selectivity of the reaction. (6) Similar effects of triphenylphosphine have been observed in stereospecific reactions with vinylic halides. (13)

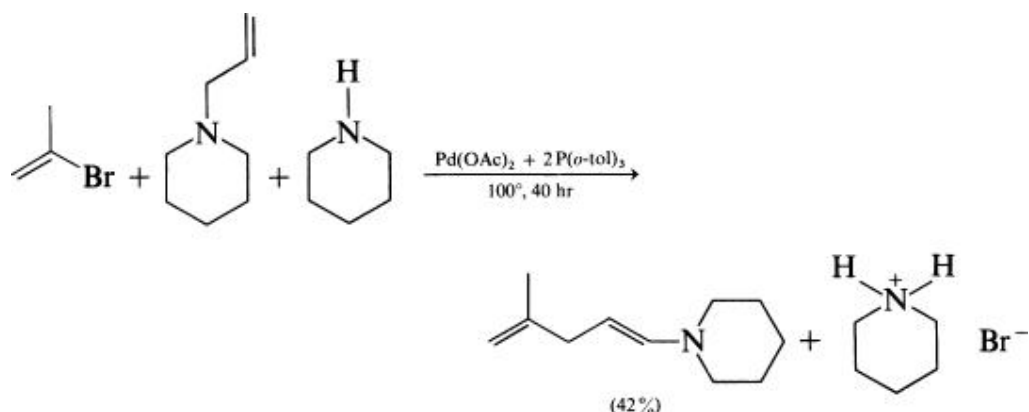
When allylic alcohols are used as the olefinic compound, carbonyl compounds are usually obtained as significant or exclusive products. (14, 15) These result from palladium hydride elimination to the beta-hydrogen atom on the hydroxyl-bearing carbon atom. Interestingly, the minor allylic alcohol-organopalladium halide adducts (with the metal added to the carbon atom gamma to the hydroxyl group) also often have given carbonyl compounds. In fact, homoallylic alcohols and alcohols with hydroxyl groups



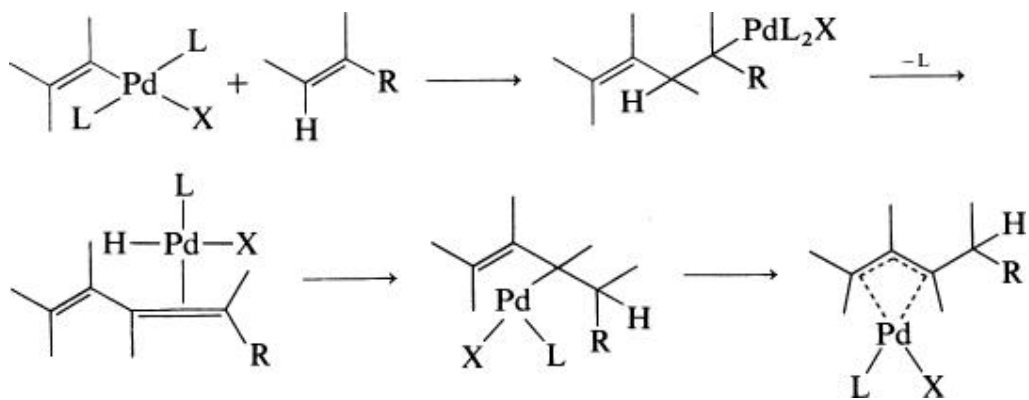
farther removed also may give significant amounts of carbonyl compounds by way of multiple elimination-readdition reactions of the hydridopalladium halide group. (15) Rates of reaction of the allylic alcohols are generally higher than those of simple olefins, suggesting that hydroxyl coordination may be involved.

Double-bond migrations are much more facile in the allylic alcohol reactions

than in the reactions of most other olefins. Of course, if unhindered secondary amines are used rather than tertiary amines as bases, aldehyde products are converted into enamines under the reaction conditions. Fortunately, these are easily hydrolyzed by dilute aqueous acid to the aldehydes. (12b) Allylic tertiary amines in the reaction may give enamines directly. (12b)

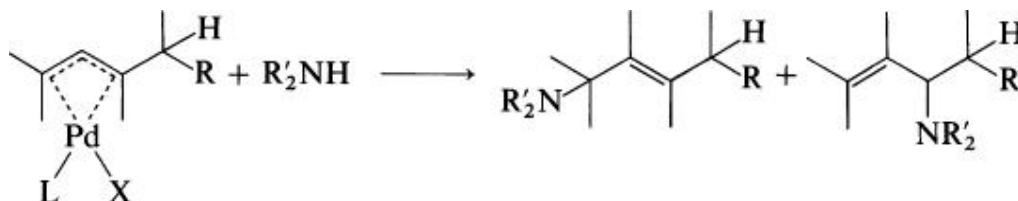


Substitution with vinylic halides as substrates may produce another complication. In these cases  $\pi$ -allylic palladium complexes are often formed by palladium hydride elimination and readdition in the reverse direction. (13, 16)

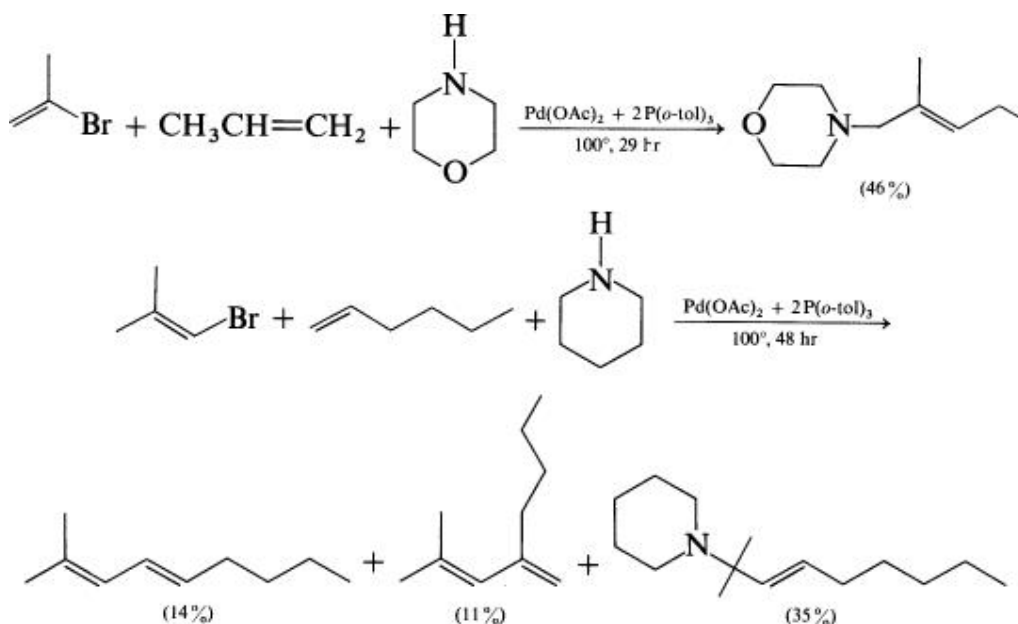


If the  $\pi$ -allylic complex undergoes palladium hydride elimination, double bond migration from the initial position may result. In many reactions the  $\pi$ -allylic complexes are sufficiently stable that they either do not decompose or do so only slowly under the usual reaction conditions with a tertiary amine as the base. Loss of palladium hydride from the  $\pi$  complexes appears to occur easily only when the R substituent in the above formulation is a carboxylate anion or ester, nitrile, or aromatic group. The  $\pi$ -allylic complexes, fortunately, are susceptible to nucleophilic attack, and the use of unhindered secondary amines as the base leads to smooth catalytic reactions with formation of

tertiary allylic amines as major products in many instances. (10) Although two isomers are possible from attack at the two terminal carbon



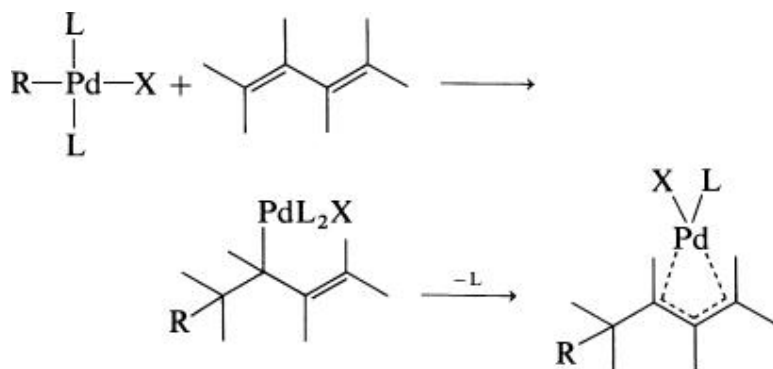
atoms of the  $\pi$ -allylic system, the reaction is often selective. The nucleophilic attack appears to be very sensitive to the steric environment about the allylic carbon atoms. The less hindered position is normally preferred with one exception. When *gem*-dimethyl substituents are present on one of the carbon atoms, this carbon is preferentially attacked. The reason for this may be that the tertiary carbon atom in a  $\pi$ -allylic system is relatively weakly bonded to the palladium and the tertiary center is more reactive to the nucleophile in an  $S_N2'$ -type reaction. (10) The N-tertiary alkyl-N,N-dialkylamines so formed are very hindered amines that do not form if groups larger than *gem*-dimethyl are present.



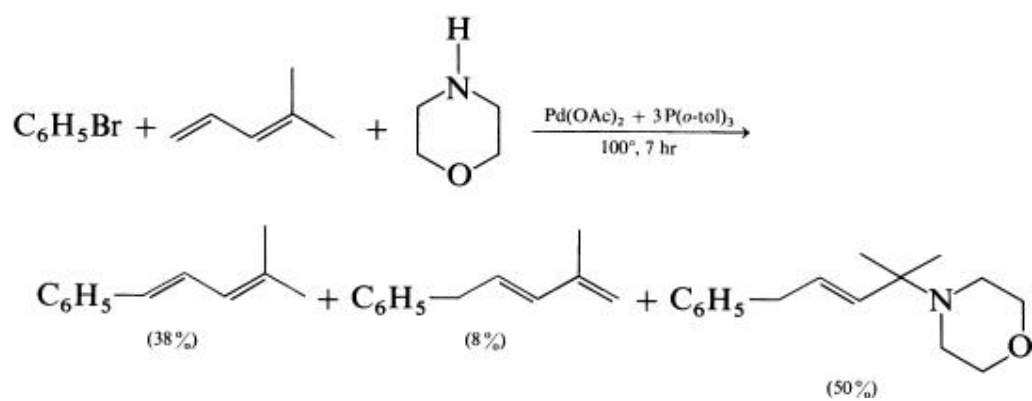
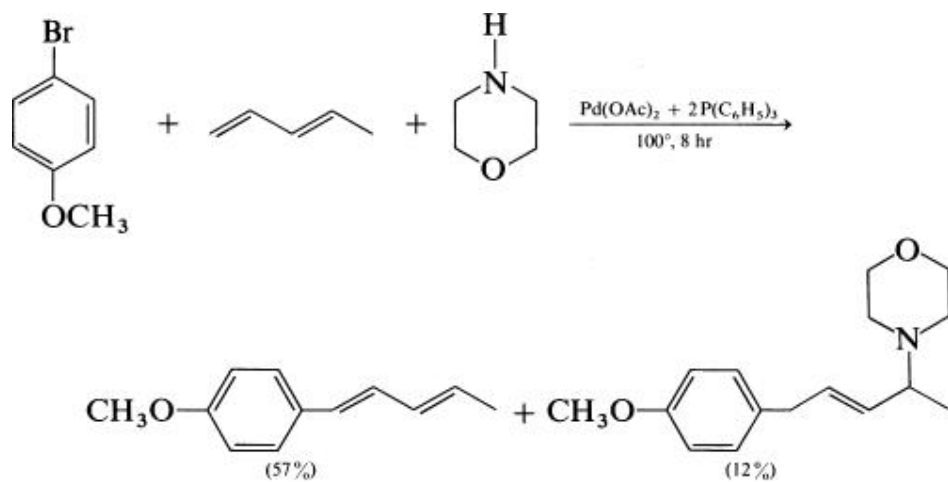
When  $\pi$ -allylic complexes are formed, the stereochemistry about the double bond of the vinylic halide is lost because there is a facile equilibration of the *syn* and *anti* forms of the  $\pi$ -allylic complexes. The preferred isomers are those having the largest allylic substituents away from the metal. Products (dienes) that are produced by elimination and loss of palladium hydride before

formation of the  $\pi$ -allylic complex retain the initial double-bond stereochemistry provided that the halide is not thermally isomerized under the reaction conditions. (10)

$\pi$ -Allylic palladium complexes may also be intermediates in the reactions of conjugated dienes with organic halides. In these reactions the  $\pi$ -allylic structure is formed directly without the need of the palladium hydride elimination and readdition. (17)



These complexes also react with nucleophilic secondary amines in the same manner as the  $\pi$ -allylic complexes formed indirectly.

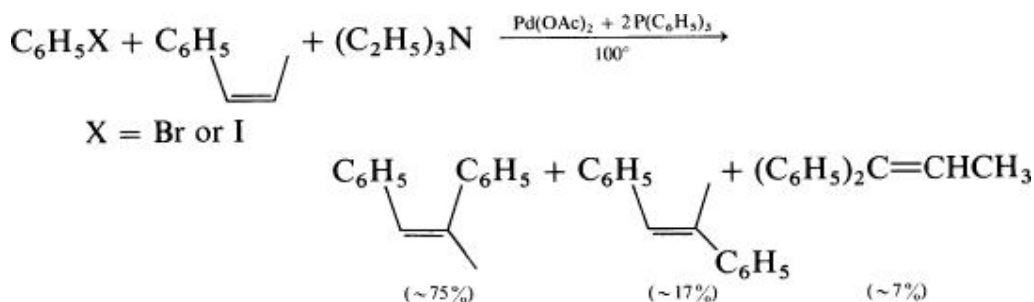


### 3. Scope and Limitations

#### 3.1. The Organic Halide

The major limitation in the organic halide is that  $sp^3$ -bonded hydrogen atoms beta to the halide group cannot be present. The palladium alkyls formed from these halides undergo palladium hydride elimination more rapidly than addition to olefins, and only elimination products are produced. Aryl, many heterocyclic, benzyl, and vinylic halides react normally. Other halides without beta  $sp^3$ -bonded hydrogen atoms exist, but for various reasons they do not react normally. Methyl halides, haloacetate esters, phenacyl bromide, and neopentyl bromide do not yield the expected products under the usual conditions. 1-Bromo-2-phenylacetylene does react normally, but a large amount of diphenylbutadiyne is also produced. (18)

A second limitation concerns the halogen atom to be used. Iodides and bromides undergo reaction comparably in most instances, with the iodides usually being a little more reactive. For example, both bromo- and iodobenzene have been made to react with *cis*-1-phenyl-1-propene at 100° in the presence of a palladium acetate–triphenylphosphine catalyst. The reaction product mixtures were essentially the same, but the iodide reacted a little more than twice as rapidly as the bromide. (6)

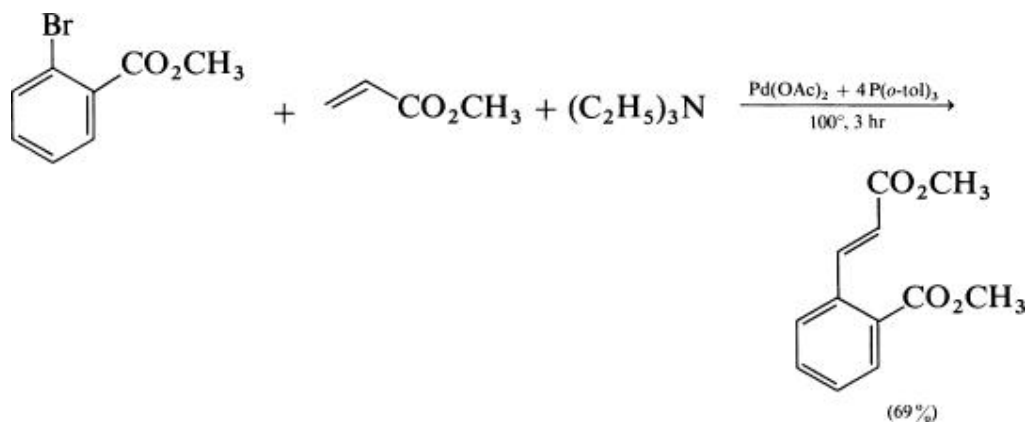


Chlorides generally do not undergo reaction. Exceptions occur when palladium on carbon is used as a catalyst with sodium carbonate as base, although yields in general are low by this method. (19) Another exception is benzyl chloride, which undergoes reaction even without a triarylphosphine. (7) Organic fluorides apparently have not been tried.

A very wide range of substituents may be present in the organic halides. (20) The only substituent known to stop the reaction in an aromatic compound is an *ortho*-carboxyl group, although the *ortho*-methyl ester reacts normally. (21) Low yields of products may be obtained when aromatic bromides containing strongly electron-donating substituents are used. The reason for the low yields



is generally that the phosphine in the catalyst is quaternized in a palladium-catalyzed reaction and/or the halide is reduced to hydrocarbon.

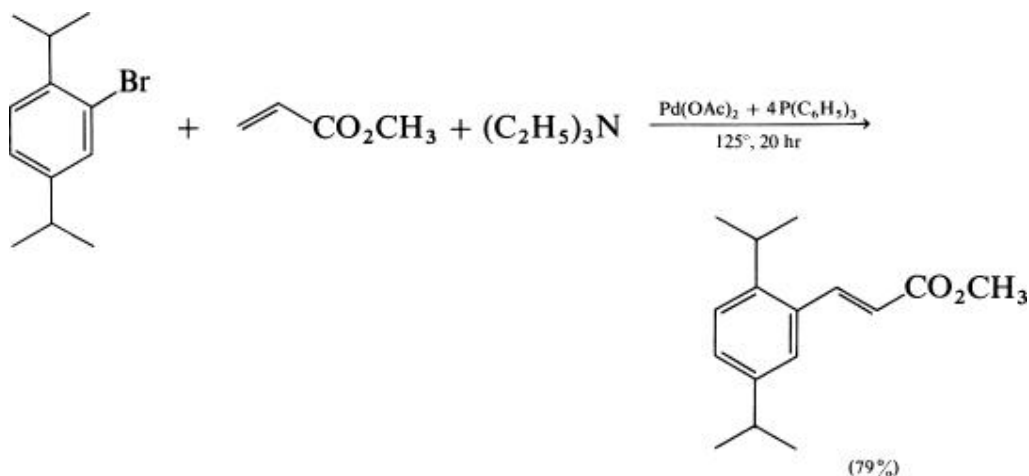


The reduction also occurs (more seriously) with similarly substituted aryl iodides. The first problem is solved by using hindered phosphines. Tri-*o*-tolylphosphine is the most generally useful one for this purpose. The success of reactions with strongly electron-donating substituents also depends on the reactivity of the olefin employed. Lower yields are obtained with the less reactive (more substituted) olefins. (20)

It should be kept in mind that triarylphosphines are not totally inert under the usual conditions for vinylation even if phosphonium salt formation does not occur. Reports of the palladium-catalyzed transfer of aryl groups from triarylphosphines to vinylic positions under the normal vinylation conditions (22) indicate that these arylated olefins may be minor side products. If this occurs, the triarylphosphine concentration is also reduced.

Quite hindered organic halides may be employed in the reaction, but reaction rates are usually low. Reaction of 2,5-diisopropylbromobenzene and methyl acrylate occurs in 79% yield at  $125^\circ$  in 20 hours, for example. (21)

Some limitations occur with heterocyclic halides as well. Successful



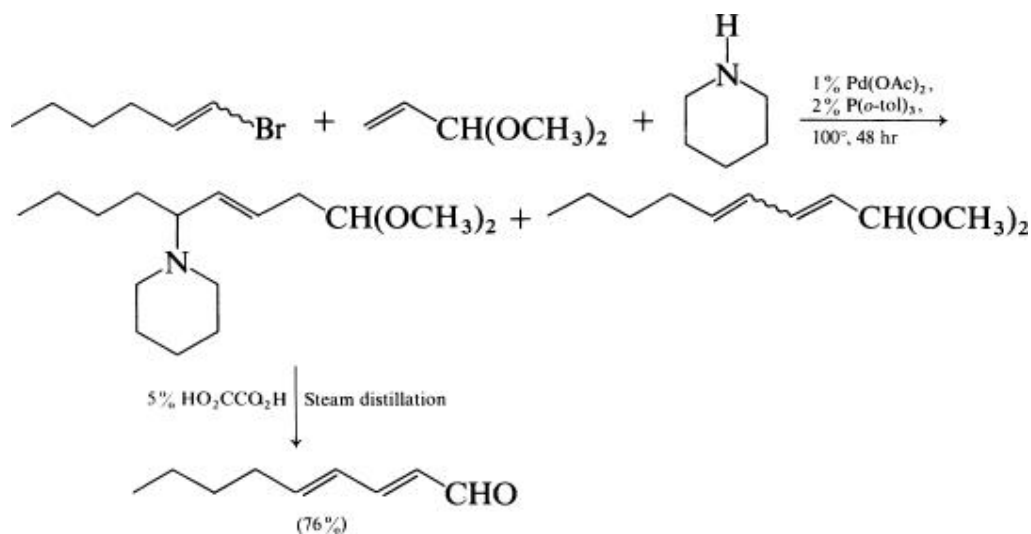
reactions occurred with methyl 5-bromofuranoate, 2- and 3-bromothiophene, 2-, 3-, and 4-bromopyridine, 2,6-dimethyl-4-bromopyridine, 3-bromoisoquinoline, 4-bromoisoquinoline, 5-bromoindole, and N-acetyl-3-bromoindole. The 2- and 4-bromopyridines react slowly and give low yields, however. Unsuccessful results were found with 3-bromoindole, 2-iodoquinoline, 2-bromothiazole, 5-bromouracil, and 4-bromo-5-phenylimidazole. (23)

A potential problem with the reactions of benzyl chloride or bromide is quaternization of both the amine base and the phosphine, if one is used. Best results are obtained with hindered amines (diisopropylethylamine) and phosphines. Vinylic halides that are activated for base-catalyzed elimination, such as methyl 2-bromoacrylate, also do not undergo the vinylic substitution reaction, presumably because elimination is favored over the substitution. Another problem appears to be the formation of vinylic tertiary amines (enamines) as minor side products in the vinylic halide–olefin–secondary amine reactions. These are apparently formed by a palladium-catalyzed alkylation of the amine with the vinylic halide. (24)

### 3.2. The Olefin

The primary factor in determining the reactivity of the olefin is the size and number of the substituents on the double-bond carbon atoms. Rates of reaction and yields of product generally decrease with increasing size and number of substituents around the double bond. Ethylene is the most reactive olefin. (25) Most monosubstituted ethylenes react well also. Even disubstituted ethylenes often react in reasonable yields but at lower rates. Poor yields are often obtained with trisubstituted ethylenes, but details have been published for only one example. (14)





Double-bond isomers often are formed when the possibility exists for elimination of different beta-hydrogen atoms. If *cis* or *trans* products are possible, the thermodynamically more stable olefin is favored. The situation is more complex when positional isomers are possible. The direction of elimination is believed to be controlled by the relative stabilities of the transition states on the way to the hydridopalladium halide–olefin  $\pi$  complexes. The various factors involved here in stabilizing the transition states are not well understood. However, it appears that the  $\pi$  complexes of the less substituted double-bond isomers are the more stable, and varying degrees of equilibration may occur during the reactions. (6) Equilibration is more rapid in the absence of a triarylphosphine than in its presence (if the reaction proceeds in its absence, see p. 360). Some isomerization may occur even in reactions when there is only one eliminatable beta hydrogen because of reverse hydride readdition and elimination of a hydrogen atom from a different carbon atom. This type of isomerization is suppressed by inclusion of a phosphine and is generally not serious. (13)

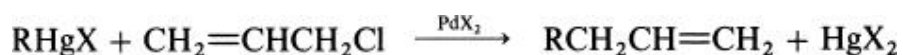
Some specific olefins that do not react well in the vinylic substitution are vinyl acetate, acrolein, and 3-buten-2-one. Vinyl acetate tends to produce mixtures of products, largely with loss of the acetate group. Both acrolein and 3-buten-2-one are often polymerized relatively rapidly under the reaction conditions. Their acetals or ketals, however, react normally. Mixtures may be obtained from acrolein acetals, however, as a result of elimination of palladium hydride in both possible directions. Allylic halides also fail in the reaction as either olefins or halides.

## 4. Comparison with Related Reactions

The Meerwein arylation reaction sometimes produces arylated olefins as products and/or the usual chloroarylated olefins. This reaction, which has been reviewed in Volumes 11 and 24 of this series, (28) is mainly limited to aryldiazonium salt reactions with activated olefins, so it does not overlap in utility to a significant extent with the vinylic substitution reaction.

More important, perhaps, are variations of the vinylic substitution with reactants other than organic halides. A reaction analogous to the Meerwein arylation occurs between aryldiazonium salts and olefins with palladium(0) catalysts. (29, 30) Vinylic substitution is the major reaction, but yields in general are lower than with the aryl halides. Yet, since many aryl halides are made from the diazonium salt, there are instances in which a one-step reaction is preferable.

Metathesis reactions between palladium(II) salts and various organometallic reagents have been widely used to produce organopalladium complexes for vinylic substitution. Organomercurials have been most extensively used. The reaction occurs under very mild conditions (0–25°) in various solvents such as acetonitrile or methanol, and yields of vinylic substitution products are generally good. (5) Advantages of this method over that employing organic halides are (a) stereospecificity is higher because of the lower reaction temperatures, (b) methyl, (5) carboalkoxy, (5) neopentyl, (31) and neophyl (31) groups can be added, and (c) allyl chloride can be used as the olefin. Also, thermally unstable materials such as substituted pyrimidin-5-yl-carbohydrates (32) and nucleosides (33) can be made by the method. In the allyl chloride reaction elimination of palladium chloride occurs in preference to the hydride so that allyl derivatives are formed catalytically. (34) The turnover



number of the palladium is only about 5 or 10, however, because some reduction of the palladium occurs in the reaction.

Disadvantages of the mercury reaction include the necessity for a stoichiometric amount of the organometallic reactant, the difficulty of obtaining many desirable mercurials, and the need for stoichiometric amounts of palladium salt for best reaction. The conversions can be made catalytic with cupric chloride as reoxidant for the palladium, but yields usually are lower and the reaction mixtures are difficult to handle because of the slurry of salts present. (5)

Other organometallics that have been used in the metathesis method include organotin, (5) organolead, (5) arylboronic acids, (13) methylcobalt complexes, (35) silanes, (36-39) Reformatsky reagents, (40) thallium alkyls, (41) and Grignard reagents. (42)

Vinylic substitution with organopalladium compounds produced by direct metalation of aromatics has been studied quite extensively. (43) Activated aromatics, including some heterocycles, metalate in an electrophilic fashion at elevated temperatures. The organopalladium compounds formed add to olefins if they are present to form vinylic substitution products. In general, yields are lower by this procedure than with organic halides. There are several serious limitations as well. The reaction is normally stoichiometric in palladium acetate. It can be made catalytic under significant oxygen pressure, but this is neither convenient nor safe. (44) The metalation may give mixtures of isomeric arylpalladium species and subsequently mixtures of vinylic substitution products. Aromatics with electron-withdrawing substituents react either poorly or not at all with palladium acetate. Many olefins are oxidized rapidly by palladium acetate relative to palladation, resulting in low yields. Thus this reaction is useful only in selected instances.

## 5. Experimental Conditions

Most vinylic substitutions have been carried out at 100° in capped bottles. The base has most often been triethylamine used in small to large molar excess over the organic halide. To achieve exclusive monosubstitution of the olefin, the olefin is generally used in small molar excess relative to the organic halide. The rates of the second substitution reaction are usually very much lower than the first, and a large excess of olefin is not necessary. The catalyst used depends on the organic halide. Generally organic iodides need only palladium acetate; bromides require palladium acetate with two or more equivalents of a triarylphosphine or an unhindered secondary amine; and chlorides only react with palladium on charcoal (except for benzyl chloride, which needs only palladium acetate). About one mole percent of palladium is normally used, based on the organic halide, to obtain convenient reaction rates at 100°. Lower amounts are often sufficient at higher reaction temperatures. Temperatures up to ca. 160° can be used before the reactions become heterogeneous, and metal is precipitated. (21)

Palladium acetate has usually been the preferred catalyst because of its relatively high solubility in organic compounds. However, other salts such as the chloride also may be used provided that the solutions are stirred to prevent the insoluble catalyst from decomposing to the metal before it dissolves and forms the "active catalyst."

Solvents may be used but often are not necessary. Excess amine is usually seen, as well as acetonitrile, methanol, dimethylformamide, N-methylpyrrolidinone, and hexamethylphosphoramide. Acetonitrile is used frequently when a triarylphosphine is not present, as in reactions of organic iodides. The finely divided palladium metal catalyst in these solutions is precipitated by the amine salt if it is allowed to crystallize from the solution. If acetonitrile is used (or probably the other solvents listed as well except triethylamine), the salt is soluble. When bases other than amines are used, certain solvents may be necessary to dissolve the bases. Sodium carbonate and bicarbonate have been used in dimethylformamide (15) and sodium acetate in methanol, (45) for example.

Reactions may be carried out in open flasks as well as capped tubes or bottles if the reactants are sufficiently high boiling or if a high-boiling solvent is used.

When triarylphosphines are present, it is preferable to carry out the reactions under nitrogen or argon to prevent oxidation of the phosphine.

It appears that the vinylic substitution is quite insensitive to impurities in the

reactants, so highly purified reagents are not necessary. Small amounts of water also do not interfere.

### 5.1. General Reaction Conditions

Standard conditions for vinylation may be in the following proportions: 10 mmol of an organic halide, 12.5 mmol of an olefin, 12.5 mmol of an amine [more amine is necessary if a free carboxyl group is present (2.5 mmol) or if secondary amines are used and allylic amines are possible products (30 mmol)], 0.10 mmol of palladium acetate, and 0.20 mmol of tri-*o*-tolylphosphine (or triphenylphosphine). The reactants are combined in a heavy-walled Pyrex tube, and the tube is capped with a self-sealing, rubber-lined cap. The mixture is then warmed in a steam bath slowly with shaking until the palladium acetate completely dissolves and a clear yellow-brown solution is obtained. The tube is then heated in the steam bath until analysis by gas chromatography of a small sample of the reaction mixture (removed by a syringe by puncturing the rubber liner of the cap via a small hole previously cut in the metal cap) shows the absence of organic halide. If triethylamine is used as the base, crystals of triethylamine hydrobromide or hydroiodide normally separate as the reaction proceeds. The products are usually recovered by adding water and filtering insoluble solid products, or by adding ether and water and extracting the product. The product extracts or solid may be washed with aqueous acid to remove excess amine, but this is usually not necessary if the product is to be recrystallized or distilled. The small amounts of palladium metal that may be present are normally easily removed by filtration in the recrystallization or before distillation. Reactants that are not soluble in the usual warm reaction mixture may be dissolved by adding a small amount of either acetonitrile or dimethylformamide. In this case the amine salts usually remain in solution. A nonaqueous work-up may also be used if the products are ether soluble. The cooled reaction mixture is diluted with excess ether, and the insoluble amine salt is removed by filtration and washed with fresh ether. The filtrates can be concentrated, and the crude products remaining can either be recrystallized or distilled directly. If the reactions are very slow at 100°, higher temperatures may be used (up to ca. 160°) or more catalyst may be added. If palladium precipitation occurs before an organic bromide completely reacts, adding additional triarylphosphine (initially), especially tri-*o*-tolylphosphine, up to ca. 6 equivalents per palladium, may keep it in solution. When allylic amines are products, it is advisable to treat the reaction mixtures with aqueous base and extract the products, since it is not always obvious whether the possible amines are present in the free or salt form.



## 6. Experimental Procedures

### 6.1.1.1. 4-Acetamidostyrene from Ethylene (25)

A mixture of 4.28 g (20 mmol) of 4-bromoacetanilide, 0.045 g (0.2 mmol) of palladium acetate, 0.122 g (0.4 mmol) of tri-*o*-tolylphosphine, 5 mL of triethylamine, and 10 mL of dimethylformamide was prepared in a 70 mL T-316 stainless-steel Parr bomb. A magnetic stirring bar was added, and the bomb was sealed and flushed with nitrogen and then with ethylene. The bomb was finally pressured to 200 psi with ethylene with stirring and then placed in a 125° oil bath. The mixture was stirred magnetically at 125° for 23 hours. After cooling and venting, the bomb was opened and the contents diluted with 100 mL of water. The solid formed was filtered and crystallized from methanol. The first fraction was (*E*)-1,2-bis(4-acetamidophenyl)ethene, 0.33 g (11%), mp > 300°. Concentration of the methanol gave on cooling 1.88 g (58%) of 4-acetamidostyrene, mp 133–136°, which was raised to 137–138° on sublimation.

In this example dimethylformamide has been used as solvent to dissolve the 4-bromoacetanilide. Only the stilbene derivative is obtained if the bromide is not in solution. A somewhat higher ethylene pressure would probably improve the yield of the styrene derivative in this case. The reaction may be inhibited by high pressure (1000 psi), however. (25)

### 6.1.1.2. 2-Bromocinnamic Acid from Acrylic Acid (46)

A solution of 2.8 g (10 mmol) of 2-bromiodobenzene, 0.9 mL (12.5 mmol) of acrylic acid, 0.022 g (0.1 mmol) of palladium acetate, 3.5 mL (25 mmol) of triethylamine, and 4 mL of acetonitrile was heated in a capped bottle at 100° in a steam bath for 1 hour. After the reaction mixture had been cooled, it was diluted with 250 mL of 10% aqueous hydrochloric acid. The solid formed was collected by filtration and recrystallized twice from ethanol (charcoal treatment) to give 1.86 g (82%) of 2-bromocinnamic acid, mp 215–216.5°.

### 6.1.1.3. 2-Carbomethoxymethyl-5-(3' -keto-1' -butyl)thiophene from 3-Buten-2-ol (47)

A mixture of 9.4 g (40 mmol) of 2-carbomethoxymethyl-5-bromothiophene, 30 mL of dimethylformamide, 4.3 g (60 mmol) of 3-buten-2-ol, 0.09 g (0.4 mmol) of palladium acetate, 3.3 g (24 mmol) of potassium carbonate and 0.31 g (1.2 mmol) of triphenylphosphine was heated at 100° for 5 hours. The cooled reaction mixture was diluted with water, and the products were separated by ether extraction. After drying and distillation, bp 155° (2 mm), there was obtained 68% of a mixture consisting of 97% 2-carbomethoxymethyl-5-(3' -keto-1' -butyl)thiophene and 3% of 2-carbomethoxymethyl-5-(2' -keto-3' -butyl)thiophene. Chromatography of

the mixture on silica gel with benzene–hexane gave 61% of a pure sample of the major product.

6.1.1.4. *(E,E)*-Dimethyl 2-Methyl-2,4-hexadienedioate from Methyl Acrylate (13)

A solution of 35.8 g (200 mmol) of (*E*)-methyl 3-bromo-2-methylpropenoate, 21.4 g (250 mmol) of methyl acrylate, 25.2 g (250 mmol) of triethylamine, 0.448 g (2.0 mmol) of palladium acetate, and 1.04 g (4.0 mmol) of triphenylphosphine was placed in a 250-mL three-necked flask equipped with a mechanical stirrer and a reflux condenser. The flask was flushed with argon and maintained under an argon atmosphere while the mixture was stirred on the steam bath for 8 hours. The cooled reaction mixture was then diluted with 300 mL of ether and filtered. The solid amine salt was washed thoroughly with another 500 mL of ether. The combined filtrates were concentrated and distilled under reduced pressure. The product, bp 89° (0.65 mm), solidified on cooling and was recrystallized from hexane. There was obtained 22 g (60%) of colorless crystals of (*E,E*)-dimethyl 2-methyl-2,4-hexadienedioate, mp 54.5–55.5°.

6.1.1.5. *(E)*-Methyl 3-(9'-Phenanthryl)acrylate from Methyl Acrylate (21)

A mixture of 2.57 g (10 mmol) of 9-bromophenanthrene, 1.1 mL (12.5 mmol) of methyl acrylate, 5 mL of triethylamine, 0.022 g (0.1 mmol) of palladium acetate, and 0.122 g (0.4 mmol) of tri-*o*-tolylphosphine was prepared in a 22-mL Pyrex tube. The tube was flushed with nitrogen, capped, and heated at 100° for 3.5 hours. After the reaction mixture had been cooled, it was diluted with 200 mL of 10% aqueous hydrochloric acid. The insoluble solid formed was collected by filtration and recrystallized from ethanol with hot filtration through Celite to remove palladium metal. There was obtained 1.89 g (72%) of colorless crystals of product, mp 98–100°. Another recrystallization from ethanol raised the melting point to 100–101°.

6.1.1.6. *(E)*-4-Cyanostilbene from Styrene (19)

A mixture of 20 mL of dioxane, 4.12 g (30 mmol) of *p*-chlorobenzonitrile, 3.12 g (30 mmol) of styrene, 3.18 g (30 mmol) of sodium carbonate, and 0.5 milliequivalent of palladium as 5% on carbon was heated at 120° for 40 hours at atmospheric pressure. Details of the product isolation were not given, but presumably dilution with water and filtration gave the crude product. A 28% yield was reported.

6.1.1.7. 2-Methyl-6-morpholino-1,4-heptadiene from (*E*)-1,3-Pentadiene (26)

In a 200-mL Pyrex bottle was placed 6.05 g (50 mmol) of 2-bromopropene, 4.25 g (62.5 mmol) of (*E*)-1,3-pentadiene, 13.1 mL (150 mmol) of morpholine, 0.112 g (0.50 mmol) of palladium acetate, and 0.30 g (1.0 mmol) of tri-*o*-tolylphosphine. This bottle was flushed with nitrogen, capped, and heated in a steam bath for 30 hours. After the reaction mixture had been cooled and

diluted with excess dilute aqueous sodium hydroxide, the product was extracted with several portions of ether. The dried extracts were concentrated and distilled. There was obtained 5.68 g of product, bp 63–76° (0.5 mm), which contained 89% (55% yield) of 2-methyl-6-morpholino-1,4-heptadiene. Two impurities were present, 4% of 2-methyl-4-morpholino-1,5-heptadiene (probably) and 3% of a morpholine–pentadiene adduct. A pure sample of the major product was obtained by preparative glc.

*6.1.1.8. 2,4-Nonadienal from Acrolein Dimethyl Acetal (12a)*

A solution of 16.3 g (0.100 mol) of 1-bromo-1-hexene [this product was mainly the (*Z*) isomer], (48) 12.5 g (0.125 mol) of acrolein dimethyl acetal, 30 mL (0.300 mol) of piperidine, 0.224 g (0.001 mol) of palladium acetate, and 0.610 g (0.002 mol) of tri-*o*-tolylphosphine was heated in a nitrogen-flushed, capped bottle in a steam bath for 16 hours. On cooling, the partly solid reaction mixture was rinsed into a dropping funnel with the aid of 200 mL of 5% oxalic acid in water. The bottle was rinsed with a little ether, and the rinsings were added to the dropping funnel. The contents of the funnel were then added dropwise to a boiling solution of 3 g of oxalic acid dihydrate in 100 mL of water in a 500-mL, three-necked flask, and the mixture was allowed to distill through a condenser attached to one neck. More water was added as necessary until 400 mL had distilled, after which the product was extracted with ether. The extracts were dried and distilled under reduced pressure to obtain 10.5 g (76%) of 2,4-nonadienal, bp 106–107° (13 mm). The nmr spectrum of the product showed that it contained *ca.* 90% of one isomer, presumably (*E,E*), and 10% of another (*E,Z?*) judging by the areas of the aldehyde proton doublets.

## 7. Tabular Survey

The following table includes all significant published examples of the palladium-catalyzed vinylic substitution reaction and some unpublished examples through December 1979. When numerous examples of the same basic reaction were reported, only the best one is given. Side products obtained in less than 5% yield are generally not shown.

Reactions are listed by increasing number of carbon atoms in the olefin. These in turn are subdivided according to the increasing number of carbons in the organic halide with iodides followed by bromides and then chlorides. Yields are based on either isolated products or gas-chromatographic data. The notes<sup>a</sup> and<sup>b</sup> at the top of each table page are explained on page 388.

**Table I. Vinylic Substitution Reactions with Organic Halides**

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TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES

No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>2</sub>	CH <sub>2</sub> =CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> I	Pd black	KOAc, CH <sub>3</sub> OH	3 hr, 125°	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub> (74)	50
		3-HOC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	19 hr, 125°	3-HOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (74)	49
		(Z)- <i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=CHI	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	139 hr, 130°	1,3-Octadiene (14), 2,4-octadiene (62)	13
		(Z)- <i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=CHI	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	88 hr, 155°	1,3-Octadiene (6), 2,4-octadiene (68)	13
		2,3-(CH <sub>3</sub> )(HO)C <sub>6</sub> H <sub>3</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	12 hr, 125°	2,3-(CH <sub>3</sub> )(HO)C <sub>6</sub> H <sub>3</sub> CH=CH <sub>2</sub> (88)	49
		3-CH <sub>3</sub> CO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	4.3 hr, 125°	3-CH <sub>3</sub> CO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (78)	49
		2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	4 hr, 125°	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CH=CH <sub>2</sub> (79)	49
		3-C <sub>2</sub> H <sub>5</sub> NBr	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	66 hr, 125°	3-C <sub>2</sub> H <sub>5</sub> NCH=CH <sub>2</sub> (52)	25
		1,2-C <sub>6</sub> H <sub>4</sub> Br <sub>2</sub>	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	15 hr, 100°	1,2-C <sub>6</sub> H <sub>4</sub> (CH=CH <sub>2</sub> ) <sub>2</sub> (78), 2-BrC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (12)	25
		2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	2 hr, 125°	2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (55), (E)-[2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=] <sub>2</sub> (5)	25
		(Z)- <i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=CHBr	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	38 hr, 130°	1,3-Octadiene (36), 2,4-octadiene (57)	13
		(Z)- <i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	2 hr, 100°	(Z)-1,3-Octadiene (5), 2-morpholino-3-octene (84), 4-morpholino-2-octene (11)	10
		(Z)- <i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	20 hr, 100°	(Z)-1,3-Octadiene (5), 2-diethylamino-3-octene (82)	10
		4-HCOC <sub>6</sub> H <sub>4</sub> Br	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	48 hr, 125°	4-HCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (53), (E)-[4-HCOC <sub>6</sub> H <sub>4</sub> CH=] <sub>2</sub> (11)	25
		3-HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	4 hr, 100°	3-HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (51), (E)-[3-HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CH=] <sub>2</sub> (12)	25
		2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	30 hr, 125°	2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (45)	25
		2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	18 hr, 125°	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (86), (E)-[2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH=] <sub>2</sub> (4)	25
		4-CH <sub>3</sub> CONHC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, DMF	23 hr, 125°	4-CH <sub>3</sub> CONHC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (59), (E)-[4-CH <sub>3</sub> CONHC <sub>6</sub> H <sub>4</sub> CH=] <sub>2</sub> (20)	25

TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES (Continued)

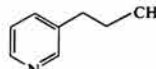
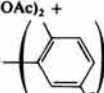
No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs		
C <sub>3</sub>	CH <sub>3</sub> CH=CH <sub>2</sub>	CH <sub>2</sub> =C(CH <sub>3</sub> )Br	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	29 hr, 100°	2-Methyl-1-morpholino-2-pentene (46)	51		
		C <sub>6</sub> H <sub>5</sub> I	Pd black	KOAc, CH <sub>3</sub> OH	3 hr, 125°	C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> (27), C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>3</sub> (73)	50		
	CH <sub>2</sub> =CHCN	(Z)-C <sub>2</sub> H <sub>5</sub> CHI=CHC <sub>2</sub> H <sub>5</sub>	Pd(OAc) <sub>2</sub> + 3 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N		22 hr, 100°	(E,Z)-4-Ethyl-2,4-heptadienenitrile (88)	27	
		C <sub>6</sub> H <sub>5</sub> I	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N		4 hr, 81-100°	(Z,Z)-4-Ethyl-2,4-heptadienenitrile (10)	14	
		2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		40 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCN (59)	20	
		C <sub>3</sub> H <sub>5</sub> FeC <sub>4</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		8 hr, 100°	(E)-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHCN (53)	52	
	CH <sub>2</sub> =CHCH <sub>2</sub> OH	3-BrC <sub>6</sub> H <sub>4</sub> N	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , HMP		9 hr, 95°	 (17)	53	
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		0.5 hr, 100°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CHO (60), CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CHO (11)	14	
		C <sub>6</sub> H <sub>5</sub> I	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N		5.5 hr, 100°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CHO (56), CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CHO (18)	14	
		C <sub>6</sub> H <sub>5</sub> I	PdBr(C <sub>6</sub> H <sub>5</sub> )[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N		26 hr, 60°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHO (56), CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CHO (18)	14	
		C <sub>6</sub> H <sub>5</sub> I	PdCl <sub>2</sub>	NaHCO <sub>3</sub> , NMP		2 hr, 130°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CHO (23), CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CHO (10)	54	
		C <sub>3</sub> H <sub>5</sub> FeC <sub>4</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		8 hr, 100°	C <sub>3</sub> H <sub>5</sub> FeC <sub>4</sub> H <sub>4</sub> CH <sub>2</sub> CHO (48)	52	
		2-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA		5 hr, 105°	2-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH <sub>2</sub> CHO (46), 2-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>3</sub> )CHO (25), 2,2'-bithienyl (8)	55	
		3-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA		19 hr, 90°	3-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH <sub>2</sub> CHO (26), 3-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>3</sub> )CHO (16)	56	
		C <sub>6</sub> H <sub>5</sub> Br	PdCl <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NMP		0.5 hr, 140°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CHO (36), CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CHO (13)	54	
		CH <sub>2</sub> =CHCO <sub>2</sub> H	2-BrC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		1 hr, 100°	(E)-2-BrC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> H (82)	46
			C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, xylene		4.5 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> H (98)	21
	C <sub>6</sub> H <sub>5</sub> Br		Pd(OAc) <sub>2</sub> + P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> <sup>f</sup>	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N		2 hr, 150°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> H (74)	21	
	2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br		Pd(OAc) <sub>2</sub> + 6 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N		12 hr, 100°	(E)-2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> H (65)	21	
	2-CH <sub>3</sub> CONHC <sub>6</sub> H <sub>4</sub> Br		Pd(OAc) <sub>2</sub> + 6 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		70 hr, 100°	(E)-2-CH <sub>3</sub> CONHC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> H (50)	49	
	CH <sub>2</sub> =CHCONH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		1 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCONH <sub>2</sub> (70)	21	
		2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		17 hr, 100°	(E)-2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHCONH <sub>2</sub> (46)	49	
		(E)-C <sub>6</sub> H <sub>5</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		4.5 hr, 100°	(E,E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHCONH <sub>2</sub> (68)	57	
	C <sub>4</sub>	CH <sub>2</sub> =CHCH=CH <sub>2</sub>	CH <sub>2</sub> =C(CH <sub>3</sub> )Br	Pd(OAc) <sub>2</sub>	Piperidine	30 hr, 100°	2-Methyl-6-piperidino-1,4-hexadiene (60)	26	
			3-C <sub>3</sub> H <sub>4</sub> NBr	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	3 hr, 100°	1-(3'-Pyridyl)-4-morpholino-2-butene (60)	60	
		CH <sub>3</sub> CH=CHCN	(CH <sub>3</sub> ) <sub>2</sub> C=CHBr	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N		340 hr, 100°	(CH <sub>3</sub> ) <sub>2</sub> C=CHC(CH <sub>3</sub> )=CHCN	13
			C <sub>6</sub> H <sub>5</sub> I	PdCl <sub>2</sub>	NaHCO <sub>3</sub> , NMP		1 hr, 130°	CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CHO (69), CH <sub>3</sub> CH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )CHO (24)	54
		(E)-CH <sub>3</sub> CH=CHCH <sub>2</sub> OH	C <sub>6</sub> H <sub>5</sub> Br	PdCl <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , HMPA		1.5 hr, 140°	CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CHO (45), CH <sub>3</sub> CH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )CHO (21)	54
			2-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA		9.5 hr, 125°	2-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>3</sub> )CH <sub>2</sub> CHO (23), 2,2'-bithienyl (52)	55
			3-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA		16 hr, 120°	3-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>3</sub> )CH <sub>2</sub> CHO (23), 3-C <sub>4</sub> H <sub>9</sub> SCH(C <sub>2</sub> H <sub>5</sub> )CHO (17)	56
		CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>2</sub> OH	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N		12 hr, 100°	CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CHO (62), CH <sub>3</sub> CH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )CHO (22)	14
			C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		1 hr, 100°	C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> CH <sub>2</sub> OH (21), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CHO (35), CH <sub>2</sub> =C(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH <sub>2</sub> OH (3), CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CHO (12)	14
C <sub>6</sub> H <sub>5</sub> I			PdCl <sub>2</sub>	NaHCO <sub>3</sub> , NMP		2 hr, 130°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CHO (44), CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CHO (13)	15	
2-C <sub>4</sub> H <sub>9</sub> SBr			Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA		3 hr, 120°	2-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (82), 2-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>3</sub> )COCH <sub>3</sub> (5)	55	
3-BrC <sub>6</sub> H <sub>4</sub> N			Pd(OAc) <sub>2</sub>	NaHCO <sub>3</sub> , DMF		5 hr, 120°	(3-C <sub>4</sub> H <sub>9</sub> N)(CH <sub>2</sub> ) <sub>2</sub> COCH <sub>3</sub> (87)	53	
CH <sub>2</sub> =CHCHOHCH <sub>3</sub>		3-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA		9 hr, 120°	3-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (90), 3-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>3</sub> )COCH <sub>3</sub> (8)	55	
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		5 hr, 100°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (86), CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )COCH <sub>3</sub> (9)	14	
		C <sub>6</sub> H <sub>5</sub> I	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N		6 hr, 100°	3-OH 3-CO 2-OH 2-CO <sup>d</sup> 13 73 4 6	14	
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub> + 8 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N		14 hr, 50°	3-OH 3-CO 2-OH 2-CO <sup>d</sup> 7 55 4 5	14	
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		10 hr, 80-88°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (85)	14	
		C <sub>6</sub> H <sub>5</sub> I	PdCl <sub>2</sub>	NaHCO <sub>3</sub> , NMP		2 hr, 130°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (89)	54	
	4-HOC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	NaHCO <sub>3</sub> , NMA, (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N		3.5 hr, 120°	4-HOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (77)	15		
	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN		12 hr, 100°	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (84)	14		

TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES (Continued)

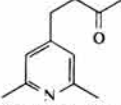
No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs.	
C <sub>4</sub> (Contd.)	CH <sub>2</sub> =CHCHOHCH <sub>3</sub>	3-C <sub>6</sub> H <sub>5</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI	10 hr, 120°	3-C <sub>6</sub> H <sub>5</sub> SCH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (90), 3-C <sub>6</sub> H <sub>5</sub> SCH(CH <sub>3</sub> )COCH <sub>3</sub> (8)	56	
		C <sub>6</sub> H <sub>5</sub> Br	PdCl <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , HMPA	3 hr, 140°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (70), C <sub>6</sub> H <sub>5</sub> CH=CHCH(OH)CH <sub>3</sub> (30)	54	
		C <sub>6</sub> H <sub>5</sub> Br	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	35 hr, 100°	3-OH 3-CO 2-OH 2-CO <sup>d</sup> 38 48 8 2	14	
		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 4 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	50 hr, 100°	3-OH 3-CO 2-OH 2-CO <sup>d</sup> 45 37 11 2	14	
		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 18 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	144 hr, 100°	3-OH 3-CO 2-OH 2-CO <sup>d</sup> 43 19 10 2	14	
		C <sub>6</sub> H <sub>5</sub> Br	PdCl <sub>2</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	30 hr, 100°	3-OH 3-CO 2-OH 2-CO <sup>d</sup> 35 47 8 2	14	
		C <sub>6</sub> H <sub>5</sub> Br	PdBr <sub>2</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	35 hr, 100°	3-OH 3-CO 2-OH 2-CO <sup>d</sup> 35 47 8 2	14	
		C <sub>6</sub> H <sub>5</sub> Br	PdI <sub>2</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	40 hr, 100°	3-OH 3-CO 2-OH 2-CO <sup>d</sup> 36 43 8 3	14	
		4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	44 hr, 100°	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH=CHCH(OH)CH <sub>3</sub> (23), 4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (64), 4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> )COCH <sub>3</sub> (1), 4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> C(=CH <sub>2</sub> )CH(OH)CH <sub>3</sub> (5)	14	
		4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	48 hr, 100°	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH=CHCH(OH)CH <sub>3</sub> (40), 4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (27), 4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> C(=CH <sub>2</sub> )CH(OH)CH <sub>3</sub> (8)	14	
		2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	2 wk, 100°	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH=CHCH(OH)CH <sub>3</sub> (64), 2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (15), 2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> C(=CH <sub>2</sub> )CH(OH)CH <sub>3</sub> (9)	14	
		4-Bromo-2,6-lutidine	Pd(OAc) <sub>2</sub>	NaHCO <sub>3</sub> , DMF	30 hr, 120°	 (65)	58	
		4-CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NMP	2 hr, 130°	4-CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (35)	15	
		CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> OH	Fe(C <sub>5</sub> H <sub>4</sub> ) <sub>2</sub>	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	Fe(C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> ) <sub>2</sub> (53)	52
			C <sub>3</sub> H <sub>5</sub> FeC <sub>3</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	C <sub>3</sub> H <sub>5</sub> FeC <sub>3</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (57)	52
2-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		NaHCO <sub>3</sub> , NaI, HMPA	8.5 hr, 105°	2-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH(CH <sub>3</sub> )CHO (42), 2,2'-bithienyl (31), 2-C <sub>4</sub> H <sub>9</sub> SCH=C(CH <sub>3</sub> )CHO (10)	55		
3-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		NaHCO <sub>3</sub> , NaI, HMPA	33 hr, 100°	3-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH(CH <sub>3</sub> )CHO (73)	55		
4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	PdCl <sub>2</sub>		NaHCO <sub>3</sub> , NMP	5.5 hr, 130°	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (50)	15		
4-HOC <sub>6</sub> H <sub>4</sub> I	PdCl <sub>2</sub>		NaHCO <sub>3</sub> , NMP	2.5 hr, 130°	4-HOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (42)	15		
C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>		(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	(CH <sub>3</sub> ) <sub>2</sub> C(C <sub>6</sub> H <sub>5</sub> )CHO (4), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (91)	14		
C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>		(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, <i>i</i> -C <sub>4</sub> H <sub>9</sub> OH	14 hr, 107-113°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (61)	14		
C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>		NaHCO <sub>3</sub> , NMP	2 hr, 130°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (95)	54		
2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	PdCl <sub>2</sub>		NaHCO <sub>3</sub> , NMP	0.7 hr, 140°	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (77)	15		
4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> I	PdCl <sub>2</sub>		NaHCO <sub>3</sub> , NMP	16.5 hr, 125°	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (61)	15		
4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> C <sub>6</sub> H <sub>4</sub> I	PdCl <sub>2</sub>		NaHCO <sub>3</sub> , NMP	6 hr, 130°	4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (95)	15		
2-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		NaHCO <sub>3</sub> , NaI, DMF	16 hr, 120°	2-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH(CH <sub>3</sub> )CHO (82), [2-C <sub>4</sub> H <sub>9</sub> S] <sub>2</sub> (9)	47		
3-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		NaHCO <sub>3</sub> , NaI, HMPA	33 hr, 100°	3-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH(CH <sub>3</sub> )CHO (79), 3-C <sub>4</sub> H <sub>9</sub> SCH=C(CH <sub>3</sub> )CHO (11)	56		
3-C <sub>4</sub> H <sub>9</sub> NBr	Pd(OAc) <sub>2</sub> + 2 POT		(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	17 hr, 100°	3-C <sub>4</sub> H <sub>9</sub> NCH <sub>2</sub> CH(CH <sub>3</sub> )CHO (64)	23		
3-BrC <sub>3</sub> H <sub>4</sub> N	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		NaHCO <sub>3</sub> , HMPA or DMF	48 hr, 100°	(3-C <sub>4</sub> H <sub>9</sub> N)CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (50)	53		
2-CH <sub>3</sub> -5-BrC <sub>4</sub> H <sub>2</sub> S	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		NaHCO <sub>3</sub> , NaI, HMPA	25 hr, 120°	2-CH <sub>3</sub> C <sub>4</sub> H <sub>2</sub> SCH <sub>2</sub> CH(CH <sub>3</sub> )CHO-5 (75), 2-CH <sub>3</sub> C <sub>4</sub> H <sub>2</sub> SC(CH <sub>3</sub> )CHO-5 (8)	47		
C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		NaHCO <sub>3</sub> , DMF	2 hr, 130°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (100)	54		
2-CH <sub>3</sub> O <sub>2</sub> CCH <sub>2</sub> -5-BrC <sub>4</sub> H <sub>2</sub> S	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		NaHCO <sub>3</sub> , NaI, HMPA	8.5 hr, 120°	2-CH <sub>3</sub> O <sub>2</sub> CCH <sub>2</sub> C <sub>4</sub> H <sub>2</sub> SCH <sub>2</sub> CH(CH <sub>3</sub> )CHO-5 (44), 2-CH <sub>3</sub> O <sub>2</sub> CCH <sub>2</sub> C <sub>4</sub> H <sub>2</sub> SC(CH <sub>3</sub> )CHO-5 (6), 2-CH <sub>3</sub> O <sub>2</sub> CCH <sub>2</sub> C <sub>4</sub> H <sub>2</sub> S (24)	47		
2-CH <sub>3</sub> O <sub>2</sub> C-5-BrC <sub>4</sub> H <sub>2</sub> S	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		K <sub>2</sub> CO <sub>3</sub> , DMF, NaI	5 hr, 100°	2-CH <sub>3</sub> O <sub>2</sub> CCH <sub>2</sub> C <sub>4</sub> H <sub>2</sub> SCH <sub>2</sub> CH(CH <sub>3</sub> )CHO-5 (61), 2-CH <sub>3</sub> O <sub>2</sub> CCH <sub>2</sub> C <sub>4</sub> H <sub>2</sub> SC(CH <sub>3</sub> )CHO-5 (3)	47		
2-CH <sub>3</sub> CO-5-BrC <sub>4</sub> H <sub>2</sub> S	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		NaHCO <sub>3</sub> , NaI, HMPA	5 hr, 120°	2-CH <sub>3</sub> COCH <sub>2</sub> C <sub>4</sub> H <sub>2</sub> S (7) 2-CH <sub>3</sub> COCH <sub>2</sub> C <sub>4</sub> H <sub>2</sub> SC(CH <sub>3</sub> )CHO-5 (80)	47		
2-CH <sub>3</sub> O <sub>2</sub> C-5-BrC <sub>4</sub> H <sub>2</sub> S	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		NaHCO <sub>3</sub> , NaI, HMPA	9 hr, 120°	2-CH <sub>3</sub> O <sub>2</sub> CC <sub>4</sub> H <sub>2</sub> SCH <sub>2</sub> CH(CH <sub>3</sub> )CHO-5 (60)	47		
4-NCC <sub>6</sub> H <sub>4</sub> Br	PdCl <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		NaHCO <sub>3</sub> , NMP	4 hr, 130°	4-NCC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (52)	15		
4-OHCC <sub>6</sub> H <sub>4</sub> Br	PdCl <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>		NaHCO <sub>3</sub> , NMP	7 hr, 130°	4-OHCC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (57)	15		

TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES (Continued)

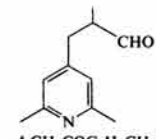
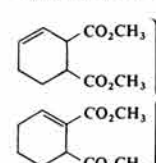
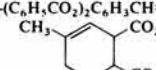
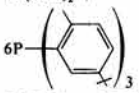
No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs.		
C <sub>4</sub> (Contd.)	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> OH	4-Bromo-2,6-lutidine	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , DMF	48 hr, 100°	 (95)	58		
		4-CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NMP	2 hr, 130°	4-CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (35)	15		
		3,4-CH <sub>2</sub> O <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Br	PdCl <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> N, DMF, NaHCO <sub>3</sub>	4 hr, 135°	3,4-CH <sub>2</sub> O <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (52)	15		
		4-C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , HMPA	0.7 hr, 130°	4-C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (82)	15		
		4- <i>i</i> -C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub>	NaHCO <sub>3</sub> , NaI, HMPA	10 hr, 110°	4- <i>i</i> -C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (72)	15		
		4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> C <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub>	NaHCO <sub>3</sub> , NaI, HMPA	4 hr, 110°	4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CHO (82)	15		
		CH <sub>2</sub> =CHOC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	3 hr, 100°	C <sub>6</sub> H <sub>5</sub> C(OC <sub>2</sub> H <sub>5</sub> )=CH <sub>2</sub> (11), ( <i>Z</i> )-C <sub>2</sub> H <sub>5</sub> OCH=CHC <sub>6</sub> H <sub>5</sub> (20) ( <i>E</i> )-C <sub>2</sub> H <sub>5</sub> OCH=CHC <sub>6</sub> H <sub>5</sub> (20)	59	
		CH <sub>2</sub> =CHCOCH <sub>3</sub>	Fe(C <sub>5</sub> H <sub>4</sub> ) <sub>2</sub>	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	Fe(C <sub>5</sub> H <sub>4</sub> )CH=CHCOCH <sub>3</sub> (76)	52	
			C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> CH=CHCOCH <sub>3</sub> (52)	52	
			CH <sub>2</sub> =CHCO <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> =CHI	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	32 hr, 100°	 (52)	13
				( <i>Z</i> )-C <sub>2</sub> H <sub>5</sub> CHI=CHC <sub>2</sub> H <sub>5</sub>	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	4 hr, 100°	Methyl ( <i>E,Z</i> )-4-ethyl-2,4-heptadienoate (86)	27
				( <i>E</i> )-C <sub>2</sub> H <sub>5</sub> CHI=CHC <sub>2</sub> H <sub>5</sub>	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	4 hr, 100°	Methyl ( <i>E,E</i> )-4-ethyl-2,4-heptadienoate (89)	27
				4-BrC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	5.5 hr, 100°	( <i>E</i> )-4-BrC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (68)	46
				C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N, (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	1 hr, 100° 21 hr, 100°	( <i>E</i> )-C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (81) (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> CH <sub>3</sub> (70)	7 21
				C <sub>6</sub> H <sub>5</sub> I	Pd black	KOAc, CH <sub>3</sub> OH	3 hr, 125°	( <i>E</i> )-C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (97)	50
		C <sub>6</sub> H <sub>5</sub> I	5% Pd/C	Na <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH	4 hr, 150°	( <i>E</i> )-C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (70)	60		
		2-HOC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> + 6 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	9 hr, 100°	( <i>E</i> )-2-HOC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (83)	21		
		3-HOC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	5 hr, 100°	( <i>E</i> )-3-HOC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (95)	21		
		2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	80 hr, 100°	( <i>E</i> )-2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> H (72)	20		
		1,2,4-H <sub>2</sub> NC <sub>6</sub> H <sub>3</sub> (1)Br	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	24 hr, 100°	( <i>E</i> )-2-H <sub>2</sub> N-5-BrC <sub>6</sub> H <sub>3</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (33)	46		
		( <i>E</i> )- <i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=CHI	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	38 hr, 100°	( <i>E,E</i> )-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH=CHCH=CHCO <sub>2</sub> CH <sub>3</sub> (45), ( <i>E,Z</i> )-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH=CHCH=CHCO <sub>2</sub> CH <sub>3</sub> (8)	13 13		
		( <i>Z</i> )- <i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=CHI	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	15 hr, 100°	<i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=CHCH=CHCO <sub>2</sub> CH <sub>3</sub> (51); ( <i>E,Z</i> ) (30)	13		
		4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	5 hr, 100°	( <i>E</i> )-4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (68)	7		
		2,4-(C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	32 hr, 100°	( <i>E</i> )-2,4-(C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (35)	20		
		CH <sub>3</sub> CBr=CH <sub>2</sub>	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	36 hr, 100°	 (63)	13		
		(CH <sub>3</sub> ) <sub>2</sub> C=CHBr	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	70 hr, 100°	( <i>E</i> )-(CH <sub>3</sub> ) <sub>2</sub> C=CHCH=CHCO <sub>2</sub> CH <sub>3</sub> (75)	6		
		( <i>E</i> )-CH <sub>3</sub> O <sub>2</sub> C(CH <sub>3</sub> )C=CHBr	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	6 hr, 100°	( <i>E,E</i> )-CH <sub>3</sub> O <sub>2</sub> CC(CH <sub>3</sub> )=CHCH=CHCO <sub>2</sub> CH <sub>3</sub> (60)	13		
		( <i>E</i> + <i>Z</i> )-C <sub>2</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CHBr	Pd(OAc) <sub>2</sub> + 3 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	24 hr, 125°	Methyl 5-methyl-2,4-octadienoate (two isomers) (77)	27		
		4-ClC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	18 hr, 100°	( <i>E</i> )-4-ClC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (93)	61		
		4-ClC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	12 hr, 100°	( <i>E</i> )-4-ClC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (54)	6		
		2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	4.5 hr, 100°	( <i>E</i> )-2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (88)	49		
		4-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 8 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	2 hr, 100°	( <i>E</i> )-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (73)	20		
		2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	23 hr, 100°	( <i>E</i> )-2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (83)	13		
		4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	7 hr, 100°	( <i>E</i> )-4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (73)	6		
		2-HOC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 6 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	28 hr, 100°	( <i>E</i> )-2-HOC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (24)	20		
		3-HOC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 6 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	7 hr, 100°	( <i>E</i> )-3-HOC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (24)	20		
		4-HOC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	22 hr, 75°	( <i>E</i> )-4-HOC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (98)	20		
		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	TMED	28 hr, 125°	( <i>E</i> )-C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (85)	6		



TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES (Continued)

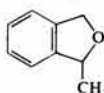
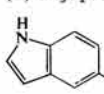
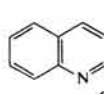
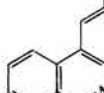
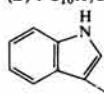
No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>4</sub> (Contd.)	CH <sub>2</sub> =CHCO <sub>2</sub> CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	43 hr, 100°	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> CH <sub>3</sub> (78)	21
		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	68 hr, 87-97°	(E)-CH <sub>2</sub> O <sub>2</sub> CCH=CHC <sub>6</sub> H <sub>5</sub> (88)	14
		(Z)-n-C <sub>4</sub> H <sub>9</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 8 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	19 hr, 100°	n-C <sub>4</sub> H <sub>9</sub> CH=CHCH=CHCO <sub>2</sub> CH <sub>3</sub> (E,E) (10); (E,Z) (82)	13
		4-NCC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	2 hr, 100°	(E)-4-NCC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (70)	21
		2-OCHC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	5.5 hr, 100°	(E)-2-OCHC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (28)	49
		4-OHCC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	18 hr, 100°	(E)-4-OHCC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (72)	21
		3-HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	5.5 hr, 100°	(E)-3-HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (67)	21
		4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	TMED	36 hr, 135°	(E)-4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (54)	6
		2-HOCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	72 hr, 100°	 (68)	21
		4-CH <sub>3</sub> SC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	72 hr, 125°	(E)-CH <sub>2</sub> O <sub>2</sub> CCH=CHC <sub>6</sub> H <sub>4</sub> SCH <sub>3</sub> -4 (77)	21
		5-Bromoindole	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	120 hr, 100°	 (53)	23
		(E)-C <sub>6</sub> H <sub>5</sub> CH=CHBr	Pd(OAc) <sub>2</sub>	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	72 hr, 100°	(E,E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHCO <sub>2</sub> CH <sub>3</sub> (47)	7
		2-CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	17 hr, 100°	(E)-2-CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (89)	49
		4-CH <sub>3</sub> CONHC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	3 hr, 100°	(E)-4-CH <sub>3</sub> CONHC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (83)	20
		2-CH <sub>3</sub> CO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 8 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	18 hr, 100°	(E)-2-CH <sub>3</sub> CO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (66)	20
		2-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	3 hr, 100°	(E)-2-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (69)	21
		4-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	37 hr, 100°	(E)-4-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (81)	6
		4-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 8 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	24 hr, 100°	(E)-4-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (80)	62
		2,4-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Br	Pd(OAc) <sub>2</sub> + 6 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	41 hr, 100°	(E)-2,4-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (13)	20
		3-Bromoquinoline	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	6 hr, 100°	 (83)	23
		4-Bromoisoquinoline	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	40 hr, 100°	 (88)	23
		1-C <sub>10</sub> H <sub>7</sub> Br	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	120 hr, 96-106°	(E)-1-C <sub>10</sub> H <sub>7</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (62)	14
		N-Acetyl-3-bromoindole	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	6 hr, 100°	 (50)	23
		2,4-(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Br	Pd(OAc) <sub>2</sub> + 8 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	4 hr, 100°	(E)-2,4-(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (26)	20
		2,5-(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Br	Pd(OAc) <sub>2</sub> + 6 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	24 hr	(E)-2,5-(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (3)	20
3,4-(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Br	Pd(OAc) <sub>2</sub> + 6 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	7 hr	(E)-3,4-(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (47)	20		
2-C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub>	TMED	65 hr, 135°	(E)-2-C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (37)	6		
2,5-[(CH <sub>3</sub> ) <sub>2</sub> CH] <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Br	Pd(OAc) <sub>2</sub> + 4 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	20 hr, 125°	(E)-2,5-[(CH <sub>3</sub> ) <sub>2</sub> CH] <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (79)	21		
9-Bromophenanthrene	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	3.5 hr, 100°	(E)-9-C <sub>14</sub> H <sub>9</sub> (CH=CHCO <sub>2</sub> CH <sub>3</sub> ) (72)	21		
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	5% Pd/C	Na <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH	4 hr, 150°	(E)-C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (8)	19		
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	Pd(OAc) <sub>2</sub>	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	15 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> (9)	7		
CH <sub>2</sub> =CHO <sub>2</sub> CCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	8 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub> (52), (E)-C <sub>6</sub> H <sub>5</sub> CH=CHOAc (10)	63	
	C <sub>6</sub> H <sub>5</sub> I	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	3 hr, 130°	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub> (14), C <sub>6</sub> H <sub>5</sub> CH=CHOAc (12), (E)-C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (18), (Z)-C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (3)	59	
	C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> CH=CHC <sub>5</sub> H <sub>4</sub> FeC <sub>5</sub> H <sub>5</sub> (38)	52	
	(E)-CH <sub>3</sub> CH=CHCO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 20 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	12 hr, 125°	(E)-C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CHCO <sub>2</sub> H (60)	21
	(E)-CH <sub>3</sub> CH=CHCO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	24 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CHCO <sub>2</sub> H (75)	49
CH <sub>2</sub> =C(CH <sub>3</sub> )CO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	24 hr, 125°	(E)-C <sub>6</sub> H <sub>5</sub> CH=C(CH <sub>3</sub> )CO <sub>2</sub> H (65)	21	

TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES (Continued)

No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>4</sub> (Contd.)	(E)-HOCH <sub>2</sub> CH=CHCH <sub>2</sub> OH	C <sub>6</sub> H <sub>5</sub> I	PdCl <sub>2</sub>	NaHCO <sub>3</sub> , NMP	0.5 hr, 130°	(95)	54
		C <sub>6</sub> H <sub>5</sub> Br	PdCl <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , HMPA	2 hr, 140°	(100)	54
C <sub>5</sub>	(E)-CH <sub>2</sub> =CHCH=CHCH <sub>3</sub>	CH <sub>2</sub> =CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	17 hr, 100°	6-Morpholino-1,4-heptadiene (18)	26
		CH <sub>2</sub> =C(CH <sub>3</sub> )Br	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	30 hr, 100°	2-Methyl-6-morpholino-1,4-heptadiene (55)	26
		(Z)-C <sub>2</sub> H <sub>5</sub> CHI=CHC <sub>2</sub> H <sub>5</sub>	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	13 hr, 100°	Undecatrienes (9), 4-ethyl-8-morpholino-3,6-nonadiene (63), morpholinoheptadecatrienes (28)	26
		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub>	Piperidine	22 hr, 100°	(E,E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHCH <sub>3</sub> (49), (E)-C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH=CHCH(CH <sub>3</sub> )NC <sub>3</sub> H <sub>7</sub> (45)	51
	CH <sub>2</sub> =C(CH <sub>3</sub> )CH=CH <sub>2</sub>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Morpholine	8 hr, 100°	(E,E)-4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CHCH=CHCH <sub>3</sub> (57), 1-p-anisyl-4-morpholino-3-pentene (12)	17
		(Z)-CH <sub>3</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	5 d, 100°	2-Methyl-1-morpholino-2,5-heptadiene (40)	26
	CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>3</sub> OH	CH <sub>2</sub> =C(CH <sub>3</sub> )Br	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	45 hr, 100°	2,5-Dimethyl-1-morpholino-2,5-heptadiene (40)	26
		(CH <sub>3</sub> ) <sub>2</sub> C=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	4 d, 100°	2,6-Dimethyl-1,3,5-heptatriene (12), 2,6-dimethyl-1-morpholino-2,5-heptadiene (54), 2,6-dimethyl-3-morpholino-1,5-heptadiene (8)	26
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	18 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHC(CH <sub>3</sub> )=CH <sub>2</sub> (52)	17
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub> + 2 POT	Piperidine	13 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHC(CH <sub>3</sub> )=CH <sub>2</sub> (22), (E)-C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> NC <sub>3</sub> H <sub>7</sub> (59)	51
C <sub>6</sub> H <sub>5</sub> Br		Pd(OAc) <sub>2</sub>	Piperidine	51 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHC(CH <sub>3</sub> )=CH <sub>2</sub> (54), (E)-C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> NC <sub>3</sub> H <sub>7</sub> (39)	51	
C <sub>6</sub> H <sub>5</sub> Br		Pd(OAc) <sub>2</sub> + 2 POT	Piperidine	48 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHC(CH <sub>3</sub> )=CH <sub>2</sub> (35), (E)-C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> NC <sub>3</sub> H <sub>7</sub> (57)	17	
CH <sub>2</sub> =CHCH <sub>2</sub> CHOHCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> I	PdCl <sub>2</sub>	NaHCO <sub>3</sub> , NMP	2 hr, 100°	C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>4</sub> CHO (30), CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )(CH <sub>2</sub> ) <sub>4</sub> CHO (12)	15	
	2-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, NMP	5 hr, 120°	2-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>2</sub> ) <sub>2</sub> COCH <sub>3</sub> (55), 2-C <sub>4</sub> H <sub>9</sub> SCH(C <sub>2</sub> H <sub>5</sub> )COCH <sub>3</sub> (14), 2-C <sub>4</sub> H <sub>9</sub> SCH=CHCH <sub>2</sub> CHOHCH <sub>3</sub> (20), 2,2'-bithienyl (8)	55	
	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub> + CH <sub>3</sub> CN	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	6.5 hr, 100°	C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> CHOHCH <sub>3</sub> (38), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (42), CH <sub>2</sub> =C(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CHOHCH <sub>3</sub> (7), CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> COCH <sub>3</sub> (9)	14	
	C <sub>6</sub> H <sub>5</sub> Br	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	24 hr, 100°	C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> CHOHCH <sub>3</sub> (58), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (6), CH <sub>2</sub> =C(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CHOHCH <sub>3</sub> (13), CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> COCH <sub>3</sub> (1)	14	
	2-CH <sub>3</sub> O <sub>2</sub> CC <sub>4</sub> H <sub>9</sub> SBr-5	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	—	2-CH <sub>3</sub> O <sub>2</sub> CC <sub>4</sub> H <sub>9</sub> S(CH <sub>2</sub> ) <sub>3</sub> COCH <sub>3</sub> -5 (28), 2-CH <sub>3</sub> O <sub>2</sub> CC <sub>4</sub> H <sub>9</sub> SCH=CHCH <sub>2</sub> CHOHCH <sub>3</sub> -5 (12)	47	
C <sub>2</sub> H <sub>5</sub> CHOHCH=CH <sub>2</sub>	2-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	2.5 hr, 120°	2-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH <sub>2</sub> COC <sub>2</sub> H <sub>5</sub> (85), 2-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>3</sub> )COC <sub>2</sub> H <sub>5</sub> (9)	55	
	3-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	16 hr, 120°	3-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH <sub>2</sub> COC <sub>2</sub> H <sub>5</sub> (80), 3-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>3</sub> )COC <sub>2</sub> H <sub>5</sub> (6), [3-C <sub>4</sub> H <sub>9</sub> S] <sub>2</sub> (5)	56	
CH <sub>2</sub> =C(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> OH	C <sub>6</sub> H <sub>5</sub> I	PdCl <sub>2</sub>	NaHCO <sub>3</sub> , NMP	7 hr, 130°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CHO (45), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (10)	15	
	C <sub>6</sub> H <sub>5</sub> I	PdCl <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NMP	3 hr, 130°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CHO (50)	15	
(E)-CH <sub>3</sub> CH=CHCHOHCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> I	PdCl <sub>2</sub>	NaHCO <sub>3</sub> , NMP	20 hr, 130°	CH <sub>3</sub> CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CHOHCH <sub>3</sub> (50)	54	
	3-BrC <sub>2</sub> H <sub>4</sub> N	Pd(OAc) <sub>2</sub>	NaHCO <sub>3</sub> , DMF	24 hr, 120°	(71), (18)	53	
	2-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	2.5 hr, 120°	2-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>3</sub> )CH <sub>2</sub> COCH <sub>3</sub> (54), 2,2'-bithienyl (20)	55	
	3-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	10 hr, 120°	3-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>3</sub> )CH <sub>2</sub> COCH <sub>3</sub> (62), 3-C <sub>4</sub> H <sub>9</sub> SCH(C <sub>2</sub> H <sub>5</sub> )COCH <sub>3</sub> (16)	56	

TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES (Continued)

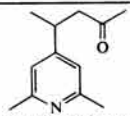
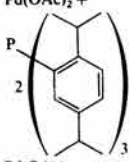
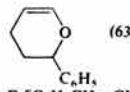
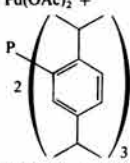
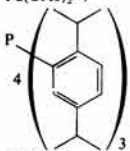
No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>5</sub> (Contd.)	(E)-CH <sub>3</sub> CH=CHCHOHCH <sub>3</sub>	4-Bromo-2,6-lutidine	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , DMF	20 hr, 120°	 (62)	58
	CH <sub>2</sub> =CHCHOHC <sub>2</sub> F <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	20 hr, 80°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> COC <sub>2</sub> F <sub>5</sub> (57), C <sub>6</sub> H <sub>5</sub> CH=CHCH(OH)C <sub>2</sub> F <sub>5</sub> (29)	64
	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> OH	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	12 hr, 100°	C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> CCH <sub>2</sub> CHO (13), (CH <sub>3</sub> ) <sub>2</sub> C=C(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> OH (9), (CH <sub>3</sub> ) <sub>2</sub> CHCH(C <sub>6</sub> H <sub>5</sub> )CHO (1), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (2)	14
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	96 hr, 100°	C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> CCH <sub>2</sub> CHO (32), (CH <sub>3</sub> ) <sub>2</sub> C=C(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> OH (10), (CH <sub>3</sub> ) <sub>2</sub> CHCH(C <sub>6</sub> H <sub>5</sub> )CHO (2), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (3)	14
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	12 hr, 100°	C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> CCH <sub>2</sub> CHO (7), (CH <sub>3</sub> ) <sub>2</sub> C=C(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> OH (13), (CH <sub>3</sub> ) <sub>2</sub> CHCH(C <sub>6</sub> H <sub>5</sub> )CHO (3), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (21)	14
		C <sub>6</sub> H <sub>5</sub> I	PdCl <sub>2</sub>	NaHCO <sub>3</sub> , NMP	10 hr, 130°	C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> CCH <sub>2</sub> CHO (36), (CH <sub>3</sub> ) <sub>2</sub> CHCH(C <sub>6</sub> H <sub>5</sub> )CHO (16)	54
		C <sub>6</sub> H <sub>5</sub> Br	PdCl <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , HMPA	4 hr, 140°	C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> CCH <sub>2</sub> CHO (27), (CH <sub>3</sub> ) <sub>2</sub> CHCH(C <sub>6</sub> H <sub>5</sub> )CHO (19), CH <sub>2</sub> =C(CH <sub>3</sub> )CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> OH (35)	54
	CH <sub>2</sub> =CHC(OH)(CH <sub>3</sub> ) <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> C=CHBr	Pd(OAc) <sub>2</sub> + 	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	72 hr, 100°	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH=CHCOH(CH <sub>3</sub> ) <sub>2</sub> (66), CH <sub>2</sub> =C(CH <sub>3</sub> )CH=CHCH <sub>2</sub> COH(CH <sub>3</sub> ) <sub>2</sub> (4), (CH <sub>3</sub> ) <sub>2</sub> C=CHC(=CH <sub>2</sub> )COH(CH <sub>3</sub> ) <sub>2</sub> (10), CH <sub>2</sub> =C(CH <sub>3</sub> )CH=C(CH <sub>3</sub> )COH(CH <sub>3</sub> ) <sub>2</sub> (2)	65
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	5 hr, 100°	C <sub>6</sub> H <sub>5</sub> CH=CHCOH(CH <sub>3</sub> ) <sub>2</sub> (8), C <sub>6</sub> H <sub>5</sub> C(=CH <sub>2</sub> )COH(CH <sub>3</sub> ) <sub>2</sub> (1), C <sub>6</sub> H <sub>5</sub> CH=CHC(CH <sub>3</sub> )=CH <sub>2</sub> (91)	14
		C <sub>6</sub> H <sub>5</sub> I	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	4 hr, 100°	C <sub>6</sub> H <sub>5</sub> CH=CHCOH(CH <sub>3</sub> ) <sub>2</sub> (97), C <sub>6</sub> H <sub>5</sub> CH=CHC(CH <sub>3</sub> )=CH <sub>2</sub> (1)	14
		C <sub>6</sub> H <sub>5</sub> I	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	6 hr, 96-105°	C <sub>6</sub> H <sub>5</sub> CH=CHCOH(CH <sub>3</sub> ) <sub>2</sub> (88)	14
		C <sub>6</sub> H <sub>5</sub> Br	PdCl <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , HMPA	4 hr, 140°	C <sub>6</sub> H <sub>5</sub> CH=CHCOH(CH <sub>3</sub> ) <sub>2</sub> (65)	54
		4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>6</sub> H <sub>17</sub> ) <sub>3</sub> N, DMF, NaHCO <sub>3</sub>	3 hr, 120°	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH=CHCOH(CH <sub>3</sub> ) <sub>2</sub> (80)	15
		4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(i-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )N, HMPA, NaHCO <sub>3</sub>	3.5 hr, 130°	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CHCOH(CH <sub>3</sub> ) <sub>2</sub> (59)	15
		4-CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(n-C <sub>12</sub> H <sub>25</sub> ) <sub>3</sub> N, NMP, NaHCO <sub>3</sub>	2.5 hr, 110°	4-CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> CH=CHCOH(CH <sub>3</sub> ) <sub>2</sub> (67)	15
Dihydropyran	C <sub>6</sub> H <sub>5</sub> I	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	3 hr, 100°	 (63)	59	
CH <sub>2</sub> =CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	Fe(C <sub>5</sub> H <sub>4</sub> ) <sub>2</sub>	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	Fe[C <sub>5</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ] <sub>2</sub> (62)	52	
	C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (54)	52	
(E)-CH <sub>3</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub>	2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	30 hr, 100°	4-Methyl-2-quinolone (55), aniline (22)	66	
CH <sub>2</sub> =C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Br	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	72 hr, 105-110°	(E)-CH <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> )C=CHCO <sub>2</sub> CH <sub>3</sub> (54)	14	
	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	18 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub> (78), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C(=CH <sub>2</sub> )CO <sub>2</sub> CH <sub>3</sub> (19)	21	
	2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	42 hr, 100°	3-Methyl-2-quinolone (24)	21	
	C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> + P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> CH=C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub> (64)	52	
	(E)-BrCH=C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub>	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	48 hr, 100°	[(E,E)-CH <sub>3</sub> O <sub>2</sub> CC(CH <sub>3</sub> )=CH] <sub>2</sub> (33), [(E,Z)-CH <sub>3</sub> O <sub>2</sub> CC(CH <sub>3</sub> )=CH] <sub>2</sub> (28)	13	
	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	22 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub> (86), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C(=CH <sub>2</sub> )CO <sub>2</sub> CH <sub>3</sub> (8)	21	
	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	22 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub> (83), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C(=CH <sub>2</sub> )CO <sub>2</sub> CH <sub>3</sub> (15)	21	
CH <sub>2</sub> =C(O <sub>2</sub> CCH <sub>3</sub> )CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	8 hr, 100°	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (24), (E)-C <sub>6</sub> H <sub>5</sub> CH=C(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub> (21), (Z)-C <sub>6</sub> H <sub>5</sub> CH=C(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub> (7), (E)-C <sub>6</sub> H <sub>5</sub> CH=C(O <sub>2</sub> CCH <sub>3</sub> )CH <sub>3</sub> (10), (Z)-C <sub>6</sub> H <sub>5</sub> CH=C(O <sub>2</sub> CCH <sub>3</sub> )CH <sub>3</sub> (2)	63	
	C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	8 hr, 100°	1,2-Diferrocenyl-1-propene (32)	52	

TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES (Continued)

No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>5</sub> (Contd.)	CH <sub>2</sub> =CHCH <sub>2</sub> NHCOCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	17 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> NHCOCH <sub>3</sub> (46)	67
	CH <sub>2</sub> =CHCH(OCH <sub>3</sub> ) <sub>2</sub>	CH <sub>2</sub> =CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Piperidine	20 hr, 100°	5-Piperidino-3-pentenal dimethyl acetal (57)	27
		CH <sub>2</sub> =C(CH <sub>3</sub> )Br	Pd(OAc) <sub>2</sub> + POT	Piperidine	22 hr, 100°	4-Methyl-2,4-pentadienal dimethyl acetal (31), 5-piperidino-4-methyl-3-pentenal dimethyl acetal (60)	27
		(E)-CH <sub>3</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Piperidine	9 hr, 100°	(E,E)-Sorbic aldehyde dimethyl acetal (23), 5-piperidino-3-hexenal dimethyl acetal (72)	27
		(Z)-CH <sub>3</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Piperidine	8 hr, 100°	(E,Z)-Sorbic aldehyde (22), 5-piperidino-3-hexenal dimethyl acetal (73)	27
		C <sub>2</sub> H <sub>5</sub> CBr=CH <sub>2</sub>	Pd(OAc) <sub>2</sub>	Morpholine	48 hr, 125°	5-Morpholino-4-ethyl-3-pentenal dimethyl acetal (84)	27
		(E)-CH <sub>3</sub> CH=C(Br)CH <sub>3</sub>	Pd(OAc) <sub>2</sub>	Morpholine	6 d, 100°	5-Morpholino-4-methyl-3-hexenal dimethyl acetal (78)	27
		(CH <sub>3</sub> ) <sub>2</sub> C=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Piperidine	18 hr, 100°	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH=CHCHO (76) <sup>c</sup>	27
		(E)-CH <sub>3</sub> O <sub>2</sub> CC(CH <sub>3</sub> )=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	12 hr, 100°	CH <sub>3</sub> O <sub>2</sub> CC(CH <sub>3</sub> )=CHCH=CHCH(OCH <sub>3</sub> ) <sub>2</sub> (70)	27
		(CH <sub>3</sub> ) <sub>2</sub> C=C(Br)CH <sub>3</sub>	Pd(OAc) <sub>2</sub> + 2 POT	Piperidine	3.5 d, 145°	4,5-Dimethyl-3,5-hexadienyl dimethyl acetal (45), 5-piperidino-4,5-dimethyl-3-hexenal dimethyl acetal (13)	27
		(E)-n-C <sub>4</sub> H <sub>9</sub> CH=CHI	Pd(OAc) <sub>2</sub>	Piperidine, CH <sub>3</sub> CN	48 hr, 100°	5-Piperidino-3-nonenal dimethyl acetal (71)	27
		(Z)-CH <sub>3</sub> (CH <sub>2</sub> )CH=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Piperidine	24 hr, 100°	2,4-Nonadienal dimethyl acetal (28), 5-piperidino-3-nonenal dimethyl acetal (60)	27
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	67 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH(OCH <sub>3</sub> ) <sub>2</sub> (8)	62
		2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	72 hr, 100°	Dihydro-2-quinolone (32), quinoline (53)	66
		4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	15 hr, 100°	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> (42)	62
	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 8 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	18 hr, 100°	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> (59)	62	
	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	24 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH(OCH <sub>3</sub> ) <sub>2</sub> (45), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> (10)	62	
C <sub>6</sub>		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	24 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH(OCH <sub>3</sub> ) <sub>2</sub> (47), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> (34)	62
		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	22 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH(OCH <sub>3</sub> ) <sub>2</sub> (56), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> (39)	62
	(E,E)-2,4-Pentadienoic acid	1,3,4-I,Cl,H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	21 hr, 100°	(E,E)-3,4-Cl(H <sub>2</sub> N)C <sub>6</sub> H <sub>4</sub> CH=CHCH=CHCO <sub>2</sub> H (42)	71
		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	20 hr, 100°	(E,E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHCO <sub>2</sub> H (92)	17
		3,4-CH <sub>2</sub> O <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Br	Pd(OAc) <sub>2</sub> + 6 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	24 hr, 100°	(E,E)-3,4-CH <sub>2</sub> O <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH=CHCH=CHCO <sub>2</sub> H (60)	17
		(E)-C <sub>6</sub> H <sub>5</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	4 hr, 100°	(E,E,E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHCH=CHCO <sub>2</sub> H (57)	17
	(E,E)-CH <sub>3</sub> CH=CHCH=CHCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	96 hr, 100°	(E)-5-Phenyl-2-morpholino-3-hexene (69)	51
		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	71 hr, 100°	(E)-5-Phenyl-2-morpholino-3-hexene (77)	51
	(E)-CH <sub>3</sub> =CHC(CH <sub>3</sub> )=CHCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	38 hr, 100°	(E,E)-C <sub>6</sub> H <sub>5</sub> CH=CHC(CH <sub>3</sub> )=CHCH <sub>3</sub> (55), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH(CH <sub>3</sub> )NC <sub>4</sub> H <sub>8</sub> O (33)	51
	CH <sub>2</sub> =CHCH=C(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine, CH <sub>3</sub> CN	10 hr, 100°	1-Phenyl-4-methyl-1,3-pentadiene (76), 5-phenyl-2-methyl-1,3-pentadiene (10)	51
		CH <sub>2</sub> =C(CH <sub>3</sub> )Br	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	22 hr, 100°	2,6-Dimethyl-1,3,5-heptatriene (12), 2,6-dimethyl-1-morpholino-2,5-heptadiene (3), 2,6-dimethyl-6-morpholino-1,4-heptadiene (26)	26
		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 3 POT	Morpholine	7 hr, 100°	1-Phenyl-4-methyl-1,3-pentadiene (38), 5-phenyl-2-methyl-1,3-pentadiene (8), 4-methyl-4-morpholino-1-phenyl-2-pentene (50)	51
	CH <sub>2</sub> =C(CH <sub>3</sub> )C(CH <sub>3</sub> )=CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	75 hr, 125°	(E)-C <sub>6</sub> H <sub>5</sub> CH=C(CH <sub>3</sub> )C(CH <sub>3</sub> )=CH <sub>2</sub> (18), C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=C(CH <sub>3</sub> )CH <sub>2</sub> NC <sub>4</sub> H <sub>8</sub> O (32)	51
	Cyclohexene	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	15 hr, 100°	3-Phenylcyclohexene (72)	66
		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	41 hr, 125°	3-Phenylcyclohexene (56)	66
	4-HOCOC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> +	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	40 hr, 125°	4-(1'-Cyclohexenyl)benzoic acid (16)	66	
1,3-Cyclohexadiene		CH <sub>2</sub> =C(CH <sub>3</sub> )Br		Piperidine	24 hr, 100°	1-Isopropenyl-1,3-cyclohexadiene (21), 3-piperidino-6-isopropenylcyclohexene (35), 3-piperidino-4-isopropenylcyclohexene (15)	26
		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Piperidine	16 hr, 100°	Phenylcyclohexadienes (13), 3-phenyl-6-piperidino-1-cyclohexene (51)	6

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TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES (Continued)

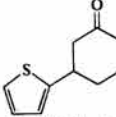
No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs.		
C <sub>6</sub> (Contd.)	<i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	22 hr, 100°	( <i>E</i> )-1-Phenyl-1-hexene (42), other phenylhexenes (40)	6		
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	56 hr, 100°	( <i>E</i> )-1-Phenyl-1-hexene (28), other phenylhexenes (37)	6		
		CH <sub>2</sub> =CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	16 hr, 100°	1-Morpholino-2-octene (84)	10		
		( <i>E</i> )-CH <sub>3</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	47 hr, 100°	2,4-Nonadiene (18), 2-butyl-1,3-pentadiene (18), 2-morpholino-3-nonene (34), 4-methyl-2-morpholino-3-octene (11)	10		
		( <i>E</i> )-CH <sub>3</sub> CH=CHBr	Pd(OAc) <sub>2</sub>	Morpholine	32 hr, 100°	2,4-Nonadiene (10), 2-butyl-1,3-pentadiene (10), 2-morpholino-3-nonene (51), 4-methyl-2-morpholino-3-octene (17)	10		
		( <i>Z</i> )-CH <sub>3</sub> CH=CHBr	Pd(OAc) <sub>2</sub>	Morpholine	30 hr, 100°	( <i>Z,E</i> )-2,4-Nonadiene (10), 2-butyl-1,3-pentadiene (10), 2-morpholino-3-nonene (52), 4-methyl-2-morpholino-3-octene (20)	10		
		( <i>Z</i> )-CH <sub>3</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	40 hr, 100°	( <i>Z,E</i> )-2,4-Nonadiene (15), 2-butyl-1,3-pentadiene (15), 2-morpholino-3-nonene (42), 4-methyl-2-morpholino-3-octene (15)	10		
		CH <sub>2</sub> =C(CH <sub>3</sub> )Br	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	68 hr, 100°	2-Methyl-1,3-octadiene (16), 2-methyl-1,4-octadiene (16), 2-methyl-1-morpholino-2-octene (64)	10		
		CH <sub>2</sub> =C(CH <sub>3</sub> )Br	Pd(OAc) <sub>2</sub> + 2 POT	Piperidine	68 hr, 100°	2-Methyl-1,3-octadiene (16), 2-methyl-1,4-octadiene (16), 2-methyl-1-piperidino-2-octene (66)	10		
		CH <sub>2</sub> =C(CH <sub>3</sub> )Br	Pd(OAc) <sub>2</sub>	Piperidine	48 hr, 100°	2-Methyl-1,3-octadiene (3), 2-methyl-1,4-octadiene (3), 2-methyl-1-piperidino-2-octene (93)	10		
		(CH <sub>3</sub> ) <sub>2</sub> C=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	48 hr, 100°	2-Methyl-2,4-nonadiene (13), 2-butyl-4-methyl-1,3-pentadiene (15), 2-methyl-2-morpholino-3-octene (31)	10		
		(CH <sub>3</sub> ) <sub>2</sub> C=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Piperidine	48 hr, 100°	2-Methyl-2,4-nonadiene (14), 2-butyl-4-methyl-1,3-pentadiene (11), 2-methyl-2-piperidino-3-octene (35)	10		
		(CH <sub>3</sub> ) <sub>2</sub> C=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	48 hr, 100°	2-Methyl-2,4-nonadiene (40), 2-butyl-4-methyl-1,3-pentadiene (50)	10		
			( <i>E</i> )-CH <sub>3</sub> O <sub>2</sub> CC(CH <sub>3</sub> )=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	20 hr, 100°	( <i>E,E</i> )-Methyl 2-methyl-2,4-nonadienoate (63), 5 unknowns (25)	10	
			C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	41 hr, 100°	( <i>E</i> )-1-Phenyl-1-hexene (44), other phenylhexenes (43)	6	
			( <i>E</i> )- <i>n</i> -C <sub>2</sub> H <sub>5</sub> CH=CHC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	15 hr, 100°	3-Phenyl-3-hexene (39), 3-phenyl-2-hexene (23)	66
			( <i>Z</i> )- <i>n</i> -C <sub>2</sub> H <sub>5</sub> CH=CHC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	112 hr, 100°	3-Phenyl-3-hexene (23), 3-phenyl-2-hexene (23)	66
				C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	120 hr, 100°	3-Phenyl-3-hexene (30), 3-phenyl-2-hexene (15)	66
			2-Cyclohexenol	2-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	9 hr, 120°	 (50)	55
			CH <sub>2</sub> =C(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>3</sub> OH	C <sub>6</sub> H <sub>5</sub> I	PdCl <sub>2</sub>	NaHCO <sub>3</sub> , NMP	13 hr, 120°	2,2'-bithienyl (25) C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> CHO (16), unsaturated C <sub>6</sub> alcohols (12), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (13)	15
		C <sub>6</sub> H <sub>5</sub> Br	PdCl <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NMP	14 hr, 100°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> CHO (27), unsaturated C <sub>6</sub> alcohols (18)	15		
	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> CHOHCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> I	PdCl <sub>2</sub>	NaHCO <sub>3</sub> , NMP	24 hr, 130°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> COCH <sub>3</sub> (48), unsaturated C <sub>6</sub> alcohols (15), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (14)	15		
		C <sub>6</sub> H <sub>5</sub> Br	PdCl <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NMP	17 hr, 120°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> COCH <sub>3</sub> (56), unsaturated C <sub>6</sub> alcohols (27)	15		
	(CH <sub>3</sub> ) <sub>2</sub> C=CHCHOHCH <sub>3</sub>	2-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	9.5 hr, 130°	2-C <sub>4</sub> H <sub>9</sub> SC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (15), 2,2'-bithienyl (40)	55		
		3-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	62 hr, 125°	3-C <sub>4</sub> H <sub>9</sub> SC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub> (22), [3-C <sub>4</sub> H <sub>9</sub> S] <sub>2</sub> (22), 3-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> COCH <sub>3</sub> (17)	56		
	(CH <sub>3</sub> ) <sub>2</sub> CHCHOHCH=CH <sub>2</sub>	2-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	5 hr, 120°	2-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH <sub>2</sub> COCH(CH <sub>3</sub> ) <sub>2</sub> (93), 2-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>3</sub> )COCH(CH <sub>3</sub> ) <sub>2</sub> (4)	55		
		3-C <sub>4</sub> H <sub>9</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	8 hr, 130°	3-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> CH <sub>2</sub> COCH(CH <sub>3</sub> ) <sub>2</sub> (87), 3-C <sub>4</sub> H <sub>9</sub> SCH(CH <sub>3</sub> )COCH(CH <sub>3</sub> ) <sub>2</sub> (3), [3-C <sub>4</sub> H <sub>9</sub> S] <sub>2</sub> (9)	56		
	CH <sub>2</sub> =C(CH <sub>3</sub> )CH(OCH <sub>3</sub> ) <sub>2</sub>	( <i>Z</i> )-CH <sub>3</sub> CH=CHBr	Pd(OAc) <sub>2</sub>	Piperidine	14 d, 100°	5-Piperidino-2-methyl-3-hexenal dimethyl acetal (57)	27		
		( <i>Z</i> )-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH=CHBr	Pd(OAc) <sub>2</sub>	Piperidine	6.5 d, 100°	2-Methyl-2,4-nonadienal <sup>c</sup> (40)	27		
	( <i>E</i> )-CH <sub>3</sub> CH=CHCH(OCH <sub>3</sub> ) <sub>2</sub>	( <i>Z</i> )-CH <sub>3</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Piperidine	4 d, 100°	5-Piperidino-3-methyl-3-hexenal dimethyl acetal (21), N-3-methyl-5-hexenylpiperidine (5)	27		

TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES (Continued)

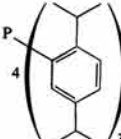
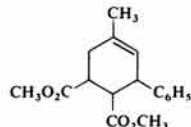
No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs.					
C <sub>6</sub> (Contd.)	CH <sub>2</sub> =CHC(O <sub>2</sub> C <sub>2</sub> H <sub>5</sub> )CH <sub>3</sub>	(Z)-CH <sub>3</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 2 POT	Piperidine	4 d, 125°	(Z,E)-3,5-Hexadien-2-one ethylene ketal (16), 6-piperidino-4-hexen-2-one ethylene ketal (47)	27					
	CH <sub>2</sub> =CHC(O <sub>2</sub> C <sub>2</sub> H <sub>4</sub> )CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	21 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHC(O <sub>2</sub> C <sub>2</sub> H <sub>4</sub> )CH <sub>3</sub> (92)	62					
	(Z)-CH <sub>3</sub> O <sub>2</sub> CCH=CHCO <sub>2</sub> CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	5 hr, 100°	CH <sub>3</sub> O <sub>2</sub> CC(C <sub>6</sub> H <sub>5</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (E) (54); (Z) (39), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (5)	66					
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	4 hr, 100°	CH <sub>3</sub> O <sub>2</sub> CC(C <sub>6</sub> H <sub>5</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (E) (43); (Z) (36), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (11)	66					
	N-Vinylpyrrolidinone		2-H <sub>2</sub> N-5-BrC <sub>6</sub> H <sub>3</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	3.5 hr, 100°	6-Bromo-4-carbomethoxy-2-quinolone (55)	66				
			2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	2 hr, 100°	4-Carbomethoxy-2-quinolone (71)	66				
			2-H <sub>2</sub> N-5-HOC <sub>6</sub> H <sub>3</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	45 hr, 100°	4-Carbomethoxy-6-hydroxy-2-quinolone (30)	66				
			4-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	17 hr, 100°	(Z)-CH <sub>3</sub> O <sub>2</sub> C(4-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (58)	66				
			C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	144 hr, 100°	(E)-CH <sub>3</sub> O <sub>2</sub> C(C <sub>6</sub> H <sub>5</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (10), (Z)-CH <sub>3</sub> O <sub>2</sub> C(C <sub>6</sub> H <sub>5</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (6)	66				
			C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	(E)-N-2-Styrylpyrrolidinone (60), (E)-N-1-styrylpyrrolidinone (40)	69				
			C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> +	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	9.5 hr, 100°	(E)-N-2-Styrylpyrrolidinone (55), (E)-N-1-styrylpyrrolidinone (44)	69				
							(E)-C <sub>6</sub> H <sub>5</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	96 hr, 100°	(E,E)-[C <sub>6</sub> NH <sub>6</sub> O]CH=CHCH=CHC <sub>6</sub> H <sub>5</sub> (25)	69
							4-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	48 hr, 100°	4-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> COCH <sub>3</sub> (57)	69
	C <sub>7</sub>	CH <sub>2</sub> =C(CH <sub>3</sub> )CH=C(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	20 d, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=CHC(CH <sub>3</sub> )=CH <sub>2</sub> (11), (E)-C <sub>6</sub> H <sub>5</sub> CH=C(CH <sub>3</sub> )CH=C(CH <sub>3</sub> ) <sub>2</sub> (30)	51				
Methyl sorbate		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	117 hr, 100°	(E,E)-C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CHCH=CHCO <sub>2</sub> CH <sub>3</sub> (34), CH <sub>3</sub> CH=CHC(CH <sub>3</sub> )=CHCO <sub>2</sub> CH <sub>3</sub> (25)	51					
Tropilidene		2-BrC <sub>6</sub> H <sub>4</sub>	Pd(OAc) <sub>2</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	100°	2-Bromophenyltropilidene (45)	70					
1-Methyl-1,3-cyclohexadiene		CH <sub>2</sub> =C(CH <sub>3</sub> )Br	Pd(OAc) <sub>2</sub>	Piperidine	20 hr, 100°	1-Isopropenyl-4-methyl-1,3-cyclohexadiene (39), unidentified triene (13), 4-isopropenyl-1-methyl-3-piperidinocyclohexene (9)	26					
2-C <sub>6</sub> H <sub>4</sub> NCH=CH <sub>2</sub>		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	136 hr, 100°	(E)-2-C <sub>6</sub> H <sub>4</sub> NCH=CHC <sub>6</sub> H <sub>5</sub> (84)	23					
4-C <sub>6</sub> H <sub>4</sub> NCH=CH <sub>2</sub>		2-C <sub>6</sub> H <sub>5</sub> SBBr	(Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	96 hr, 100°	(E)-4-C <sub>6</sub> H <sub>4</sub> NCH=CHC <sub>6</sub> H <sub>5</sub> S-2 (57)	23					
CH <sub>2</sub> =C(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> CHOHCH <sub>3</sub>		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	240 hr, 100°	(E)-4-C <sub>6</sub> H <sub>4</sub> NCH=CHC <sub>6</sub> H <sub>5</sub> (91)	23					
		C <sub>6</sub> H <sub>5</sub> I	PdCl <sub>2</sub>	NaHCO <sub>3</sub> , NMP	22.5 hr, 130°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> COCH <sub>3</sub> (40), unsaturated C <sub>7</sub> alcohols (25), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (15)	15					
		C <sub>6</sub> H <sub>5</sub> Br	PdCl <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NMP	7.5 hr, 120°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> COCH <sub>3</sub> (49), unsaturated C <sub>7</sub> alcohols (23)	15					
C <sub>8</sub>		<i>n</i> -C <sub>3</sub> H <sub>7</sub> CH=CHCH=CHCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	87 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )CH=CHCH(NC <sub>6</sub> H <sub>5</sub> O)(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> (26), (E)-C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )CH(NC <sub>6</sub> H <sub>5</sub> O)CH=CH(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> (26), 2-phenyloctadienes (30)	51				
	(E)-(CH <sub>3</sub> ) <sub>2</sub> C=CHCH=CHCO <sub>2</sub> CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	51 hr, 100°	(CH <sub>3</sub> ) <sub>2</sub> C=CHCH=C(C <sub>6</sub> H <sub>5</sub> )CO <sub>2</sub> CH <sub>3</sub> (95)	51					
	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	1,4-C <sub>6</sub> H <sub>4</sub> I <sub>2</sub>	Pd(OAc) <sub>2</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	15 hr, 100°	(E,E)- <i>p</i> -Distyrylbenzene (67)	7					
		1,2-C <sub>6</sub> H <sub>4</sub> I <sub>2</sub>	Pd(OAc) <sub>2</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	72 hr, 100°	(E,E)- <i>o</i> -Distyrylbenzene (37)	7					
		4-BrC <sub>6</sub> H <sub>4</sub> I	(Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	17 hr, 100°	(E)-4-BrC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (64)	17					
		C <sub>6</sub> H <sub>5</sub> I	Pd black	KOAc, CH <sub>3</sub> OH	3 hr, 125°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (90), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CH <sub>2</sub> (10)	50					
		C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	2 hr, 100°	(E)-Stilbene (75)	7					
		2-H <sub>2</sub> N-5-HOC <sub>6</sub> H <sub>3</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	5 hr, 100°	(E)-2-H <sub>2</sub> N-5-HOC <sub>6</sub> H <sub>3</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (50)	21					
		4-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	2 hr, 100°	(E)-4-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (74)	7					
		Fe(C <sub>5</sub> H <sub>4</sub> ) <sub>2</sub>	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	Fe(C <sub>2</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (42)	52					
	C <sub>3</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	C <sub>3</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (59)	52						
	CH <sub>2</sub> =CBrCH <sub>3</sub> + (Z)-CH <sub>3</sub> O <sub>2</sub> CCH=CHCO <sub>2</sub> CH <sub>3</sub>	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	96 hr, 100°		13						

TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES (Continued)

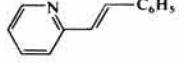
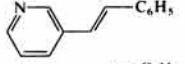
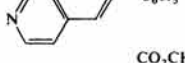
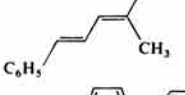
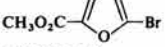
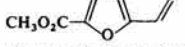

No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub> (Contd.)	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> C=CHBr	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> -Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	300 hr, 100°	(E)-(CH <sub>3</sub> ) <sub>2</sub> C=CHCH=CHC <sub>6</sub> H <sub>5</sub> (58)	13
		2-C <sub>5</sub> H <sub>4</sub> NBr	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	240 hr, 100°	 (19)	23
		3-C <sub>5</sub> H <sub>4</sub> NBr	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	20 hr, 100°	 (78)	23
		4-C <sub>5</sub> H <sub>4</sub> NBr·HCl	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	240 hr, 100°	 (41)	23
		(E)-BrCH=C(CH <sub>3</sub> )CO <sub>2</sub> CH <sub>3</sub>	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	21 hr, 100°	 (78)	13
			Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	18 hr, 100°	CH <sub>3</sub> O <sub>2</sub> C-  (61)	23
		4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	40 hr, 100°	(E)-4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (75)	61
		2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 8 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	2 hr, 100°	(E)-2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (73)	20
		4-HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	3.5 hr, 100°	(E)-4-HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (74)	21
		4-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	8 hr, 100°	(E)-4-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (77.5)	6
		3,4-HCO(HO)C <sub>6</sub> H <sub>3</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	9 hr, 100°	(E)-3,4-OHC(HO)C <sub>6</sub> H <sub>3</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (57)	57
		(E)-C <sub>6</sub> H <sub>5</sub> CH=CHBr	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	135 hr, 100°	(E,E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHC <sub>6</sub> H <sub>5</sub> (49)	13
		(E)-CH <sub>3</sub> O <sub>2</sub> CCH=CHC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	2 hr, 100°	(E,E)-4-CH <sub>3</sub> O <sub>2</sub> CCH=CHC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (63)	17
		(Z)-2-HO <sub>2</sub> CCH=CHC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	44 hr, 100°	(E,E)-2-C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> H (20)	17
		4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Cl	5% Pd/C	Na <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH	4 hr, 150°	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (50)	19
		C <sub>6</sub> H <sub>5</sub> Cl	5% Pd/C	Na <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH	4 hr, 150°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (46)	19
		4-HOC <sub>6</sub> H <sub>4</sub> Cl	5% Pd/C	Na <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH	4 hr, 150°	(E)-4-HOC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (20)	19
		4-NCC <sub>6</sub> H <sub>4</sub> Cl	5% Pd/C	Na <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH	4 hr, 150°	4-NCC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (28)	19
		4-F <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> Cl	5% Pd/C	Na <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH	4 hr, 150°	(E)-4-F <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (11)	19
		C <sub>8</sub>	2-BrC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub>	4-HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> Cl	5% Pd/C	Na <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH	4 hr, 150°
4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> Cl	5% Pd/C			Na <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH	4 hr, 150°	(E)-4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (12)	19
4-CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> Cl	5% Pd/C			Na <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH	4 hr, 150°	4-CH <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (19)	19
4-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> Cl	5% Pd/C			Na <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH	4 hr, 150°	4-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (21)	19
2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> l	Pd(OAc) <sub>2</sub>			(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	49 hr, 100°	(E)-2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>4</sub> Br-2 (73)	46
C <sub>6</sub> H <sub>5</sub> l	Pd(OAc) <sub>2</sub>			( <i>n</i> -C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> N	2hr, 100°	(E)-4-Nitrostilbene (85)	7
C <sub>6</sub> H <sub>5</sub> l	Pd(OAc) <sub>2</sub> + 4 POT			(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	24 hr, 100°	C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CHCH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (50), C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (30)	62
C <sub>6</sub> H <sub>5</sub> l	Pd(OAc) <sub>2</sub>			(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	0.5 hr, 100°	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CC(C <sub>6</sub> H <sub>5</sub> )=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (E) (19); (Z) (75), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (5)	66
C <sub>6</sub> H <sub>5</sub> l	Pd(OAc) <sub>2</sub> + 2 POT			(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	2 hr, 100°	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CC(C <sub>6</sub> H <sub>5</sub> )=CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> (E) (6); (Z) (80), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (11)	66
2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> l	Pd(OAc) <sub>2</sub>			(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	48 hr, 100°	4-Carboxy-2-quinolone (47), aniline (20)	66
(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>3</sub>	Pd(OAc) <sub>2</sub>			( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	2 hr, 100°	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHCH <sub>3</sub> (21), (E)-1,2-Diphenyl-1-propene (26)	7
C <sub>6</sub> H <sub>5</sub> l	Pd(OAc) <sub>2</sub>			(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	34 hr, 100°	(Z)-1,2-1 (E)-1,2-1 2,3-1 1,1-1 <sup>f</sup>	6
C <sub>6</sub> H <sub>5</sub> l	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>			(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	34 hr, 100°	2 44 12 27 0 71 0 29	6
C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>			(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	43 hr, 100°	0 79 0 22	6
C <sub>6</sub> H <sub>5</sub> l	Pd(OAc) <sub>2</sub>			( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	2 hr, 100°	7 12 4 -	7
C <sub>6</sub> H <sub>5</sub> l	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	34 hr, 100°	11 48 19 6	6		
C <sub>6</sub> H <sub>5</sub> l	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	142 hr, 60°	(Z)-1,2-1 (E)-1,2-1 2,3-1 1,1-1 64 13 0 5 71 14 2 7	6		
C <sub>6</sub> H <sub>5</sub> l	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	34 hr, 100°	67 17 0 7	6		
C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	33 hr, 100°	6 53 19 0	6		
C <sub>6</sub> H <sub>5</sub> l	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	33 hr, 100°	4 69 5 0	6		
(Z)-CH <sub>3</sub> CH=CHBr	Pd(OAc) <sub>2</sub> + 2 P(2-CH <sub>3</sub> -5-CF <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	72 hr, 100°	C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CHCH=CHCH <sub>3</sub> (40)	61		
C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	33 hr, 100°	(Z)-1,2-1 (E)-1,2-1 2,3-1 1,1-1 3 58 5 0	6		
C <sub>9</sub>	CH <sub>2</sub> =CHCHOHC <sub>6</sub> H <sub>5</sub>	3-BrC <sub>5</sub> H <sub>4</sub> N	Pd(OAc) <sub>2</sub>	NaHCO <sub>3</sub> , DMF	24 hr, 120°	 (91)	53
		2-C <sub>4</sub> H <sub>3</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	4 hr, 120°	2-C <sub>4</sub> H <sub>3</sub> SCH <sub>2</sub> CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (88), 2,2'-bithienyl (5)	55
		3-C <sub>4</sub> H <sub>3</sub> SBr	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	9 hr, 120°	3-C <sub>4</sub> H <sub>3</sub> SCH <sub>2</sub> CH <sub>2</sub> COC <sub>6</sub> H <sub>5</sub> (83), 3,3'-bithienyl (9)	55

TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES (Continued)

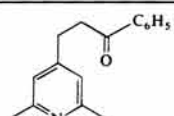
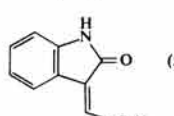
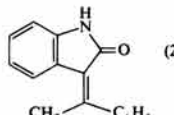
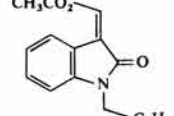
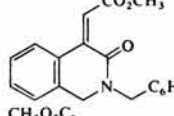
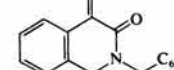
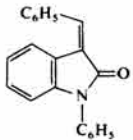
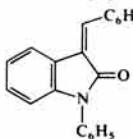
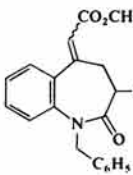
No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs.	
C <sub>6</sub> (Contd.)	CH <sub>2</sub> =CHCHOHC <sub>6</sub> H <sub>5</sub>	4-Bromo-2,6-lutidine	Pd(OAc) <sub>2</sub> + 3 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	NaHCO <sub>3</sub> , NaI, HMPA	9 hr, 120°	 (90)	58	
	CH <sub>2</sub> =CHCH(OH)C <sub>6</sub> F <sub>13</sub>	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	20 hr, 80°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> COC <sub>6</sub> F <sub>13</sub> (53), C <sub>6</sub> H <sub>5</sub> CH=CHCH(OH)C <sub>6</sub> F <sub>13</sub> (34)	71	
	2-HOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	1.5 hr, 100°	2-HOC <sub>6</sub> H <sub>4</sub> CH=CHCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (53), 2-HOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (37)	72	
	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Cl	5° Pd/C	Na <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> OH	4 hr, 150°	(E)-4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (28)	19	
	C <sub>6</sub> H <sub>5</sub> COCH=CH <sub>2</sub>	C <sub>5</sub> H <sub>3</sub> FeC <sub>3</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	C <sub>5</sub> H <sub>3</sub> FeC <sub>3</sub> H <sub>4</sub> CH=CHCOC <sub>6</sub> H <sub>5</sub> (70)	52	
	C <sub>6</sub> H <sub>5</sub> SCH=CHCH <sub>3</sub> CH <sub>2</sub> =C(C <sub>6</sub> H <sub>5</sub> )CO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> Br 2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Pd(OAc) <sub>2</sub>	TMED, CH <sub>3</sub> CN (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	3-4 d, reflux 25 hr, 100°	C <sub>6</sub> H <sub>5</sub> SCH=C(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub> (49-65) 3-Phenyl-2-quinolone (20), (E)-3- <i>o</i> -aminophenyl-2-phenylacrylic acid (41)	73 49	
	(E)-2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	27 hr, 100°	4-Phenyl-2-quinolone (71)	66	
	C <sub>6</sub> H <sub>5</sub> CH=CHO <sub>2</sub> CCH <sub>3</sub> CH <sub>2</sub> =C(O <sub>2</sub> CCH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> I C <sub>6</sub> H <sub>5</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	8 hr, 100° 8 hr, 100°	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (58) (E)-C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (36), (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (36), C <sub>6</sub> H <sub>5</sub> C(O <sub>2</sub> CCH <sub>3</sub> )=CHC <sub>6</sub> H <sub>5</sub> (20)	63 63	
	C <sub>6</sub> H <sub>5</sub> C(O <sub>2</sub> CCH <sub>3</sub> )=CH <sub>2</sub>	C <sub>5</sub> H <sub>3</sub> FeC <sub>3</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	8 hr, 100°	C <sub>5</sub> H <sub>3</sub> FeC <sub>3</sub> H <sub>4</sub> CH=CHC <sub>6</sub> H <sub>5</sub> (21), C <sub>5</sub> H <sub>3</sub> FeC <sub>3</sub> H <sub>4</sub> CH=C(O <sub>2</sub> CCH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> (14)	52	
	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> I 4-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	98 hr, 100° 53 hr, 150°	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> CH <sub>3</sub> (67) (Z)-4-HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> C(C <sub>6</sub> H <sub>5</sub> )=CHCO <sub>2</sub> H <sup>r</sup> (52)	66 66	
386 C <sub>10</sub>	Myrcene	BrCH=C(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> OH	Pd(OAc) <sub>2</sub> + 2 POT	Morpholine	2 d, 100°	3,11-Dimethyl-7-morpholinomethyl-3,6,10-dodecatrien-1-ol (41)	12b	
	2-CH <sub>2</sub> =C(CH <sub>3</sub> )CONHC <sub>6</sub> H <sub>4</sub> Br	—	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	15.5 hr, 100°	4-Methyl-2-quinolone (43)	49	
	N-Vinylphthalimide	2-BrC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	20 hr, 100°	N-2- <i>o</i> -Bromostyrylphthalimide (75)	69	
		2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	45 hr, 100°	Indole (26)	69	
		4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 2 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	17 hr, 100°	N-2- <i>p</i> -Nitrostyrylphthalimide (64)	69	
		C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	108 hr, 100°	N-2-Styrylphthalimide (74)	69	
		4-CH <sub>3</sub> CO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br	Pd(OAc) <sub>2</sub> + 8 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	18 hr, 100°	N-2- <i>p</i> -Acetoxystyrylphthalimide (75)	69	
		3,4-(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Br	Pd(OAc) <sub>2</sub> + 6 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	15 hr, 100°	N-2-(3',4'-Diacetoxystyryl)phthalimide (68)	69	
	C <sub>11</sub>	(E)-4-CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CH=CHCO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> Br	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	56 hr, 150°	4-HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> C(C <sub>6</sub> H <sub>5</sub> )=CHCO <sub>2</sub> H <sup>r</sup> (Z) (77); (E) (10)	66
	C <sub>12</sub>	3-Butenylphthalimide	3-C <sub>5</sub> H <sub>4</sub> NBr	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	10 hr, 100°	(E)-3-C <sub>5</sub> H <sub>4</sub> NCH=CHCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> (37)	23
C <sub>13</sub>	2-BrC <sub>6</sub> H <sub>4</sub> N(COCH <sub>3</sub> )CH <sub>2</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub>	—	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	TMED, DMF	5 hr, 125°	Methyl N-acetyl-3-indolylacetate (43), 2-BrC <sub>6</sub> H <sub>4</sub> NHCOCH <sub>3</sub> (29), C <sub>6</sub> H <sub>5</sub> NHCOCH <sub>3</sub> (16)	74	
C <sub>15</sub>	(Z)-C <sub>6</sub> H <sub>5</sub> CH=CHCONHC <sub>6</sub> H <sub>5</sub>	2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	19 hr, 100°	4-Phenyl-2-quinolone (66)	66	
	(E)-C <sub>6</sub> H <sub>5</sub> CH=CHCONHC <sub>6</sub> H <sub>5</sub>	2-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	Pd(OAc) <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	31 hr, 100°	4-Phenyl-2-quinolone (15)	66	
	(E)-2-C <sub>6</sub> H <sub>5</sub> CH=CHCONHC <sub>6</sub> H <sub>4</sub> Br	—	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	17.5 hr, 100°	 (58)	49	
387 C <sub>16</sub>	(E)-2-C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )=CHCONHC <sub>6</sub> H <sub>4</sub> Br	—	Pd(OAc) <sub>2</sub> + 4 POT	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	29 hr, 100°	 (22)	49	
C <sub>18</sub>	(Z)-2-BrC <sub>6</sub> H <sub>4</sub> N(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )COCH=CHCO <sub>2</sub> CH <sub>3</sub>	—	Pd(OAc) <sub>2</sub> + P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	6 hr, 70°	 (48)	75	
C <sub>19</sub>	(Z)-2-BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> N(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )COCH=CHCO <sub>2</sub> CH <sub>3</sub>	—	Pd(OAc) <sub>2</sub> + P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N, C <sub>6</sub> H <sub>5</sub> CN	3 hr, 125°	 (29),  (19)	75	



TABLE I. VINYLIC SUBSTITUTION REACTIONS WITH ORGANIC HALIDES (Continued)

No. of C Atoms	Olefin	Halide	Catalyst <sup>a</sup>	Base and Solvent <sup>b</sup>	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>21</sub>	( <i>E</i> )-2-BrC <sub>6</sub> H <sub>4</sub> N(C <sub>6</sub> H <sub>5</sub> )COCH=CHC <sub>6</sub> H <sub>5</sub>	—	PdCl <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CN) <sub>2</sub> + P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N, CH <sub>3</sub> CN	6 hr, 70°	 (13),  (60)	75
C <sub>22</sub>	2-BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> N(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub>	—	Pd(OAc) <sub>2</sub> + 2 P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	TMED	69 hr, 125°	4-Benzylisoquinoline (27), N-phenyl-4-benzylideneisoquinoline (8)	74
C <sub>23</sub>	( <i>E</i> )-2-BrC <sub>6</sub> H <sub>4</sub> N(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )COCH(CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> )CH <sub>2</sub> CH=CHCO <sub>2</sub> CH <sub>3</sub>	—	Pd(OAc) <sub>2</sub> + P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N, C <sub>6</sub> H <sub>5</sub> CN	6 hr, 120°	 (38)	75

<sup>a</sup> Pd(OAc)<sub>2</sub> = Pd(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> and POT = P(*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>.

<sup>b</sup> NMP = N-methylpyrrolidinone, HMPA = hexamethylphosphoramide, NMA = N-methylacetamide, TMED = N,N,N',N'-tetramethylethylenediamine, DMF = N,N-dimethylformamide.

<sup>c</sup> 0.05% Pd(OAc)<sub>2</sub> was used.

<sup>d</sup> 3-OH is C<sub>6</sub>H<sub>5</sub>CH=CHCHOHCH<sub>3</sub>, 3-CO is C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>COCH<sub>3</sub>, 2-OH is CH<sub>2</sub>=C(C<sub>6</sub>H<sub>5</sub>)CHOHCH<sub>3</sub>, and 2-CO is CH<sub>3</sub>CH(C<sub>6</sub>H<sub>5</sub>)COCH<sub>3</sub>.

<sup>e</sup> The yield was obtained after acidic hydrolysis.

<sup>f</sup> (*Z*)-1,2-1 is (*Z*)-1,2-diphenyl-1-propene, (*E*)-1,2-1 is (*E*)-1,2-diphenyl-1-propene, 2,3-1 is 2,3-diphenyl-1-propene, and 1,1-1 is 1,1-diphenyl-1-propene.

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