

Addition and Substitution Reactions of Nitrile-Stabilized Carbanions

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1. Introduction

The utilization of carbanions stabilized by various electron-withdrawing groups to effect carbon-carbon bond formation occupies a central position in organic synthesis. This chapter focuses on the reactions of nitrile-stabilized carbanions with an array of carbon electrophiles and updates another chapter along these lines in this series. (1) Subsequent review articles have dealt with various aspects of the chemistry of nitrile-stabilized carbanions. (2-11) In this review, the reactions of nitrile-stabilized anions are grouped according to the nature of the substituents attached to the carbanion center bearing the nitrile group. These substituents include alkyl, alkenyl, alkynyl, and aryl groups as well as various α -oriented halogen-, oxygen-, nitrogen-, sulfur-, and selenium-containing groups. Notably absent from this survey are the carbanions derived from active methylene compounds bearing two electron-withdrawing groups such as cyanoacetate esters, malononitriles, α -sulfonylnitriles, and α -phosphorylnitriles. (12, 13) Also absent are those carbanions such as Reissert compounds, which are the subject of comprehensive reviews. (14-16)

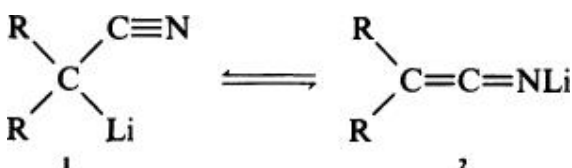
The chapter is arbitrarily subdivided into six sections: (1) reactions of alkyl-, aryl-, and heteroaryl-substituted nitriles; (2) reactions of α , β - and β , γ -unsaturated nitriles as well as tolunitriles; (3) reactions of cyanohydrins and their hydroxyl-protected derivatives; (4) reactions of nitriles bearing α -sulfur and α -selenium substituents; (5) reactions of α -(dialkylamino)nitriles; and (6) reactions of α -halonitriles. Within each of these sections, the reactions are further subdivided according to the nature of the electrophile: (1) alkylation reactions employing alkyl halides, alkyl sulfonates, dialkyl sulfates, and epoxides; (2) arylation reactions involving the substitution of hydrogen, halogen, nitro, or alkoxy groups on aryl or heteroaryl substrates; (3) acylation reactions employing carboxylic esters, anhydrides, acid chlorides, dialkyl carbonates, and nitriles; (4) addition reactions involving aldehydes, ketones, imines, alkenes, and alkynes; and (5) Michael-type addition reactions to unsaturated aldehydes, ketones, imines, sulfoxides, sulfones, and nitro compounds. Finally, a section involving cyclization reactions is included for each of the six groups of nitrile-stabilized anions.

2. Mechanism

2.1. General Considerations

2.1.1.1. Generation of Monoanions of Nitriles

Successful addition and substitution reactions of nitriles depend critically on the generation of the nitrile-stabilized carbanion represented typically by the tautomeric structures **1** and **2**.



The frequent appearance of such tautomeric representations in the literature implies a structural uniformity for nitrile-stabilized carbanions that over-simplifies the actual situation. Moreover, the aggregation state of metalated nitriles varies with structure: the lithioacetonitrile species is tetrameric whereas lithiophenylacetonitrile is dimeric in dimethyl sulfoxide. (17) Consistent with the existence of various tautomeric structures for certain nitrile-stabilized carbanions, infrared (IR) studies of the lithium (17-20) or sodium (19, 21) derivatives of acetonitrile display absorptions in the 2000–2200-cm⁻¹ region that are ascribed to the metalated ketenimine tautomer **2**. Other possible tautomeric structures (MCH = C = NH, MC ≡ CNH₂, and HC ≡ CNMH) are also suggested, (19) and both infrared and nuclear magnetic resonance (NMR) assignments are offered as supporting evidence. In contrast, the metalated derivatives of the substituted nitriles, isobutyronitrile (19) and phenylacetonitrile, (17, 20-22) display single IR absorptions at 2000 and 2080 cm⁻¹, respectively, which was interpreted to indicate the presence of a single tautomer **1** having a carbon – metal bond.

Deprotonation of primary or secondary nitriles with an array of different bases constitutes the most convenient method for generating the monoanions of nitriles. For this reason, a brief discussion of the influence of structural variations on the acidity of weak carbon acids generally, and nitriles specifically, is appropriate. The effect of common electron-withdrawing groups on the stability of carbanions and hence on the acidity of the conjugate acids decreases in the following order: NO₂ ≥ RCO > RSO₂ > CN. (23, 24) This particular order derives, however, from measurements made in dimethyl sulfoxide. Since solvent exerts a substantial influence on apparent acidities by altering the stability and aggregation states of ion pairs, (25, 26) this relative ordering of weak carbon acids may be different in another solvent. For example, in benzene or ether, acetophenone is a stronger acid than fluorene by about 6 pK_a units, whereas in dimethyl sulfoxide fluorene is a stronger acid

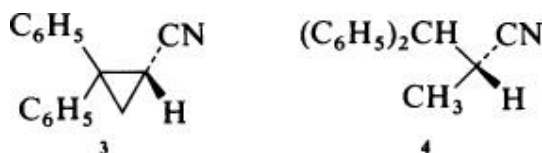
by approximately 2 pK_a units. (26) Similarly, the apparent pK_a values of phenylacetylene in ether, (27) cyclohexylamine, (25) and dimethyl sulfoxide (26) increase dramatically. Since detailed studies of the acidity of various nitriles are available only in dimethyl sulfoxide solution, the following discussion focuses on comparisons in this solvent.

Although acetonitrile (pK_a 31.3) (24) is a relatively weak acid in comparison to other carbon acids bearing electron-withdrawing groups, various substituents exert a dramatic influence on pK_a values. The introduction of additional electron-withdrawing substituents such as phenyl groups substantially lowers the pK_a values as shown in the following trend: 9-cyanofluorene (pK_a 8.3), (24) diphenylacetonitrile (pK_a 17.5), (28) phenylacetonitrile (pK_a 21.9), (28) and acetonitrile (pK_a 31.3). (24, 28) The magnitude of the pK_a differential between phenylacetonitrile and acetonitrile is considerably greater than the ΔpK_a for phenyl substitution in nitromethane or acetophenone. (28) This large differential in the acetonitrile series is ascribed to less of the negative charge residing at the nitrogen atom in the acetonitrile anion than at the more electronegative oxygen atom in the nitromethane and acetophenone anions. The addition of a second phenyl group exerts a less dramatic effect, presumably as a result of steric inhibition of resonance. (28) Other aryl- or heteroaryl-substituted acetonitriles possess acidities comparable to phenylacetonitrile: 1-naphthylacetonitrile (pK_a 20.8), (29) 2-naphthylacetonitrile (pK_a 20.6), (29) 2-thienylacetonitrile (pK_a 21.1), (29) and 2-furylacetonitrile (pK_a 21.3). (29)

In contrast to phenyl groups, methyl substitution in acetonitrile decreases the acidity of nitriles as illustrated by comparison of acetonitrile (pK_a 31.3) and propionitrile (pK_a 32.5) or phenylacetonitrile (pK_a 21.9) and 2-phenylpropionitrile (pK_a 23.0). (30) This destabilizing influence originates in the polar electron release from methyl relative to hydrogen to the sp^2 carbon in the anion. (30) This result parallels the suggested decrease in the rate of deprotonation of nitriles: $CH_3CN > CH_3CH_2CN > (CH_3)_2CHCN$ (31) and contrasts with the inverse relationship for rates of proton abstraction and acidity for similarly substituted nitromethanes. (32-34) Such findings underscore the difficulties in assigning relative carbanion stabilities from kinetic measurements alone.

The influence of ring size on the acidity of cycloalkanecarbonitriles remains unclear with the exception of the cyclopropyl series. Rehybridization from sp^3 to sp^2 necessary for delocalization of the negative charge introduces considerable strain in cyclopropyl rings (35) and diminishes the acidity of various cyclopropyl systems bearing electron-withdrawing groups. (36) Consonant with this observation is the high degree of retention observed for (-)-(R)-2,2-diphenylcyclopropanecarbonitrile (3) in the presence of sodium

alkoxides under conditions where an acyclic analog, (+)-(*R*)-2-methyl-3,3-diphenylpropionitrile (**4**), undergoes complete racemization. (**37**) The energy barrier to rehybridization in cyclopropylcarbonitriles is not, however, prohibitively high since racemization is noted using strong bases such as lithium diisopropylamide in aprotic media. (**38**)



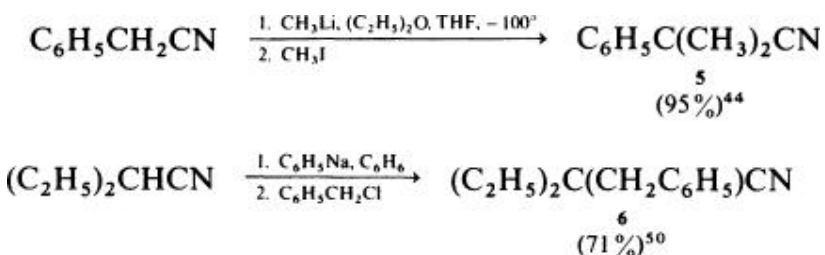
The degree to which heteroatom substituents at the α position of nitriles alter the acidity of acetonitriles varies dramatically. In general, nitriles bearing α -sulfur substituents are more acidic than nitriles bearing α -oxygen or α -halogen substituents, which, in turn, are more acidic than nitriles bearing α -nitrogen substituents. Evidence for this assertion is, in part, found in the following series: $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{CN}$ ($\text{p}K_a$ 12.0), (**39**) $\text{C}_6\text{H}_5\text{SCH}_2\text{CN}$ ($\text{p}K_a$ 20.8), (**40**, **41**) and $\text{C}_6\text{H}_5\text{OCH}_2\text{CN}$ ($\text{p}K_a$ 28.1). (**40**) Unfortunately, data bearing on the influence of halogen or dialkylamino substituents on equilibrium acidities of substituted nitriles are not as yet available, and the suggested general trend for the influence of these heteroatoms is extrapolated from analogous ketone and sulfone systems. (**40**)

The selection of an appropriate base guarantees a high concentration of the requisite nitrile-stabilized carbanion and thwarts various side reactions that intervene when the nitrile and its anion coexist in solution. Since the $\text{p}K_a$ of the nitriles considered in this chapter span over 20 $\text{p}K_a$ units, the base is usually selected to reflect the acidity range of the nitrile substrates under consideration. In general, the most acidic nitriles include the arylacetonitriles and their heteroaromatic counterparts for which weak bases, particularly sodium hydroxide under phase-transfer conditions, are adequate for the deprotonation task. The less acidic aliphatic nitriles generally require the alkali metal amide and metal alkyl reagents as bases.

Sodium and lithium hydrides react slowly with active methylene compounds bearing only one electron-withdrawing group and thus find application only in the alkylation of arylacetonitriles. The convenience of handling these hydride reagents relative to sodium amide offsets the lower yields of alkylated products occasionally encountered with the use of sodium hydride rather than sodium amide. (**42**) Application of sodium hydride to the alkylation of aliphatic acetonitriles leads to extensive polymerization under the usual heterogeneous conditions. The very reactive potassium hydride also fails to deprotonate

aliphatic acetonitriles and, in the case of 3-phenylpropionitriles, results in dehydrocyanation to give styrenes. (43)

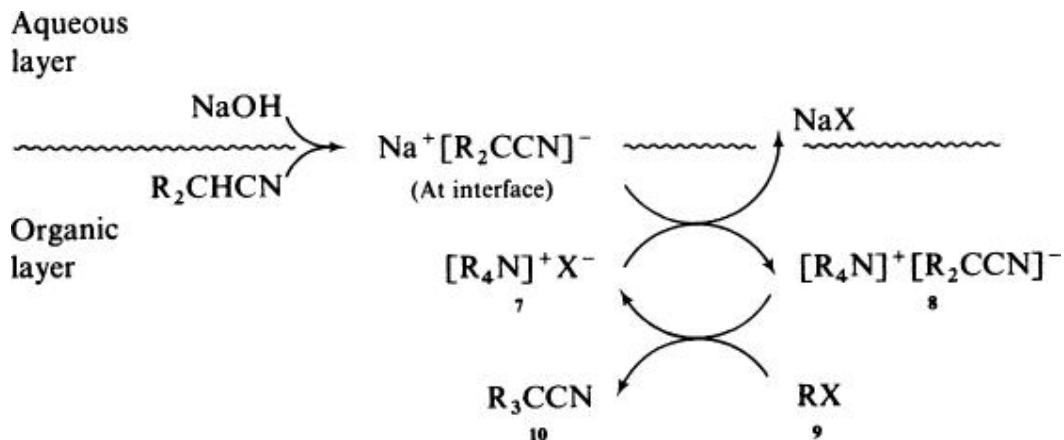
Alkyl metal reagents, including methyllithium, (44, 45) *n*-butyllithium, (46-49) *tert*-butyllithium, (19) phenylsodium, (50) methylmagnesium iodide, (51, 52) isopropylmagnesium chloride, (31) and *n*-butylmagnesium bromide, (31) are occasionally used to metalate nitriles. Their use may be complicated by competitive addition of the organometallic reagent to the nitrile moiety. The ratio of deprotonation to addition is a function of both the alkyl portion and the counterion in the organometallic reagent. For the reagents C₆H₅M, the ratio of deprotonation to addition appears to decrease in the order K > Na > Li > MgX in reactions of phenylacetonitrile or mesitylacetonitrile. (53) In general, successful alkylations using organometallic reagents as bases involve the preparation of tertiary nitriles and employ low temperatures to avoid competitive addition reactions as illustrated by the preparation of 5 (44) and 6. (50)



A number of different alkoxide bases are used for the alkylation and acylation of arylacetonitriles. Although hindered alkoxides such as potassium *tert*-butoxide are employed successfully in alkylations using alkyl halides, sodium amide is superior to sodium methoxide or sodium ethoxide in terms of yields and reaction times (54) in reactions of alkyl halides with nitriles. The use of alkali metal hydroxides is confined to reactions of aromatic or heteroaromatic acetonitriles and yet, despite this limitation, has found widespread application in nitrile reactions.

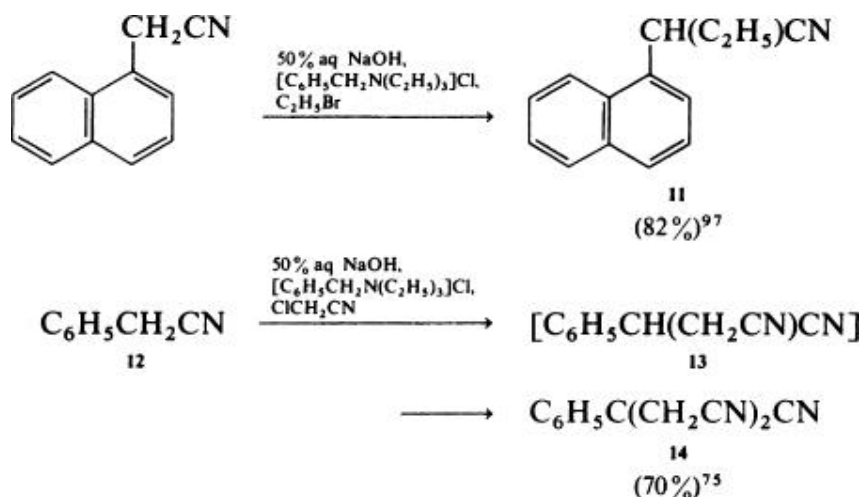
The increased acidity of such arylacetonitriles has led to the development of "phase-transfer" catalysis (7, 8, 55-63) for alkylation, (64-81) arylation, (82-87) and even vinylation (88-90) of arylacetonitriles. The mechanism (91-95) of the catalytic process for relatively weak acids such as nitriles is suggested to involve proton abstraction and formation of an ion pair at the interface. The ammonium salt acts as a carrier to transfer the nitrile-stabilized anion into the organic phase where reaction of 8 with an electrophile 9 provides the product

10 and regenerates the catalyst **7**. This mechanism contrasts with earlier suggestions that the



phase-transfer catalyst serves to transport the hydroxide ion from the aqueous layer to the organic layer where deprotonation of the nitrile would occur. In the absence of a phase-transfer catalyst, successful alkylations in a two-phase medium involve reaction at the interface. (92)

In general, phase-transfer alkylations involve the exposure of the active methylene compound to a mixture of alkylating agent, 50% aqueous sodium hydroxide, and a tetraalkylammonium salt, commonly benzyltriethylammonium chloride. As a consequence of using alkali metal hydroxides in either phase transfer or homogeneous reactions, (96) only arylacetonitriles and heteroarylacetonitriles are useful alkylation substrates as illustrated by the ethylation of 1-naphthylacetonitrile to give the monoalkylated product **11**. (97) Both monoalkylation and dialkylation are possible depending on the molar ratio of reactants and the structure of the nitrile anion and the alkylating agent. For example, the alkylation of phenylacetonitrile with chloroacetonitrile in which the ratios of the two reagents are varied over the range 1:2 to 3:1 leads exclusively to the dialkylated product **14**, (75) reflecting the greater nucleophilicity of the anion of **13** than that of **12**. In phase-transfer alkylations, alkyl chlorides are usually preferred over alkyl bromides or alkyl iodides, in contrast to the usual experience with alkylations in aprotic homogeneous media. (98) The use of polymer-bound ammonium salts as the catalytic species (99) in three-phase catalysis appears to offer no advantage over the two-phase, soluble ammonium salt procedure in terms of either yields or monoalkylation and dialkylation ratios.



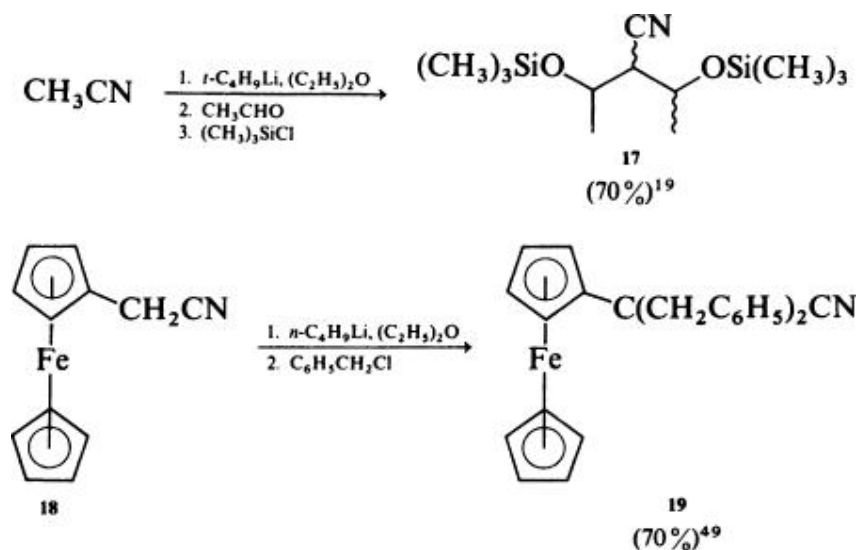
The alkali metal amides remain among the most popular of the bases for alkylation, arylation, and acylation of a broad range of primary and secondary nitriles. Although dialkylamides were first employed for the alkylation of nitriles almost 50 years ago, (100) there has been a renewed interest in their use in recent years. In part, this interest reflects the fact that the bulky dialkylamide reagents avoid side reactions such as the amidine formation (54, 100, 101) encountered with the use of simple amides and, in addition, avoid the necessity for working with liquid ammonia. A survey of the tabulated examples suggests that substituted amide bases are the reagents of choice for the generation of nitrile-stabilized monoanions.

2.1.1.2. Generation of Polyions of Nitriles

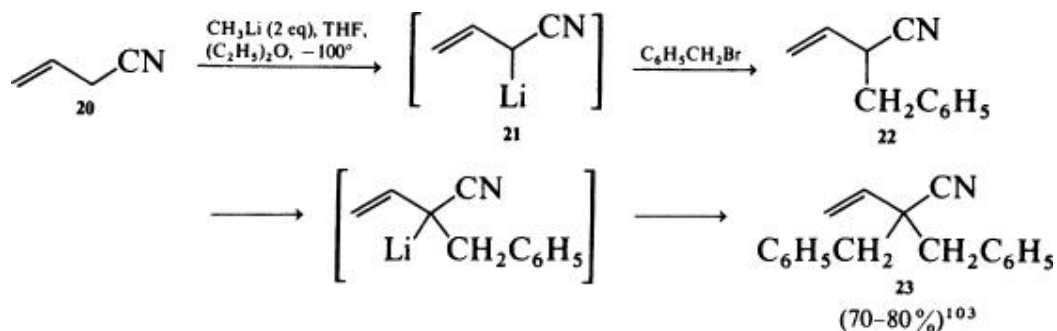
The various dianion species derived from the dimetalation of nitriles can be arbitrarily classified as geminal, vicinal, or distal for delineation of the relative location of the carbanion centers. The generation of "geminal" dianions requires a strong base to effect the second deprotonation, and as a consequence, most studies are restricted to the use of alkyllithium reagents as bases. For example, the dimetalation of acetonitrile with *tert*-butyllithium generates the geminal dianion as evidenced by the evolution of two molar equivalents of isobutane and by the IR spectrum of the metalated intermediate. (19) The "geminal" label applied to the dianion is a misnomer in that the dilithiated ketenimine **16** is a more accurate structural representation than the geminal dianion **15**, but this terminology persists.



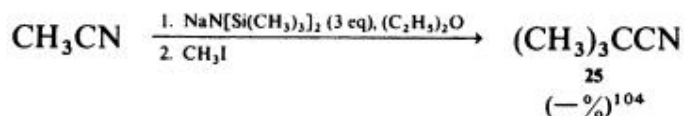
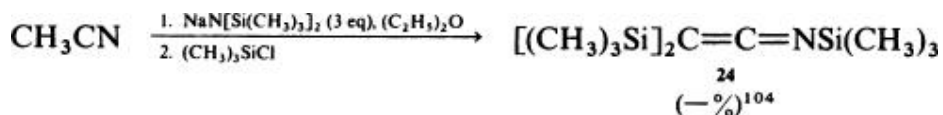
Additional evidence consistent with dianion intermediates involves the isolation of dialkylated products from reactions with either alkyl halides or carbonyl compounds. For example, the condensation of dilithioacetonitrile with acetaldehyde provides the bis adduct **17**, (19) and the alkylation of the dilithio derivative of cyanomethylferrocene (**18**) with benzyl chloride leads to the dialkylated product **19**. (49) Analogous dialkylations involving phenylacetonitrile (46, 47) or 3,4-dimethoxyphenylacetonitrile (102) are also attributed to dilithiated nitriles, but such experiments do not exclude a stepwise alkylation of the nitrile through



monoanion intermediates, and this latter pathway appears to intervene in the dialkylation of 3-butenitrile, (44, 103) phenylacetonitrile, (44) and 1-naphthylacetonitrile. (44) Exposure of 3-butenitrile (**20**), for example, to two equivalents of methyllithium leads only to the monoanion **21** according to the NMR spectrum. (44, 103) The rate of reaction of the alkylating agent benzyl bromide with the excess methyllithium is low relative to the metalation of the monoalkylated product **22**, and hence the dialkylated material **23** predominates. (103)

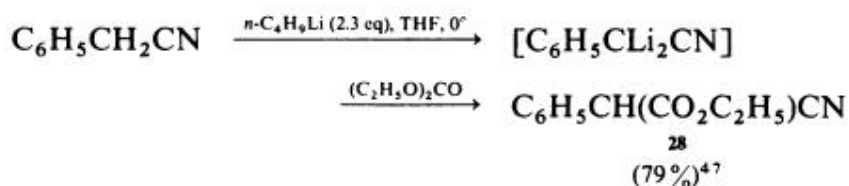
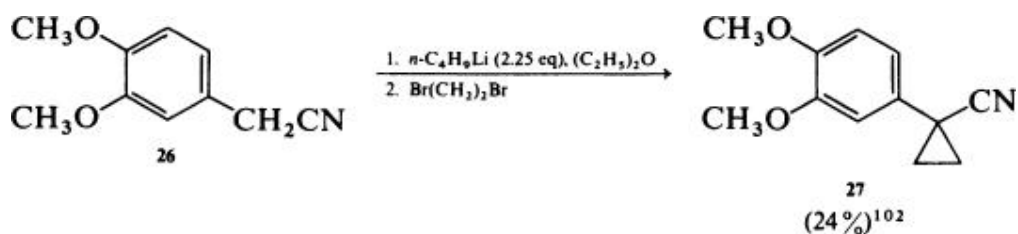


This same caution regarding the use of product analyses as mechanistic probes applies to the apparent trimetalation of acetonitrile. The intermediacy of a trimetalated acetonitrile, prepared using either sodium bis(trimethylsilyl)-amide (104, 105) or *n*-butyllithium (106) is suggested by the isolation of the tris(trimethylsilyl)ketenimine (24) and pivalonitrile (25) from reactions with chlorotrimethylsilane and methyl iodide, respectively. Reinvestigation (19) of these reactions revealed that a monometalated acetonitrile is the principal organometallic species produced, and the products arise from sequential alkylation and deprotonation. As yet, conclusive evidence for a trimetalated acetonitrile derivative in solution is not available.

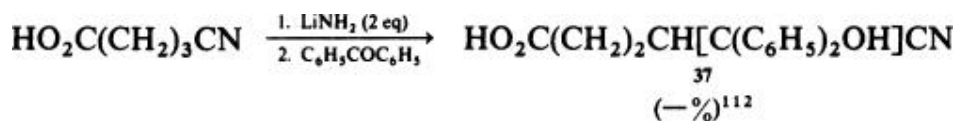


Synthetic applications of geminal nitrile dianions are limited by the requirement for alkyllithium reagents needed for their generation and by the availability of alternative procedures involving nitrile monoanions that often reach the same objectives. The dilithiated derivative of 3,4-dimethoxyphenylacetonitrile (26) furnishes the cyclopropane 27, for example, in only 24% yield, (102) whereas the sequential dialkylation of 26 through monolithiated intermediates gives 27 in 86% yield. (107) Nevertheless, other dialkylations of dilithio derivatives of phenylacetonitrile lead to synthetically useful yields of cyclic products. (47) The acylation of the dianion of phenylacetonitrile with diethyl carbonate also provides an improved yield of the cyanoester 28 relative to the acylation of the

monoanion, where the highly acidic product competes for the monoanion intermediate. (47)

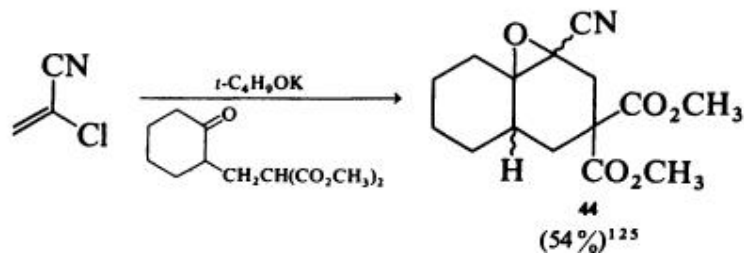
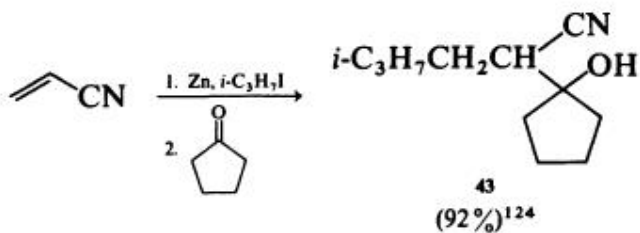
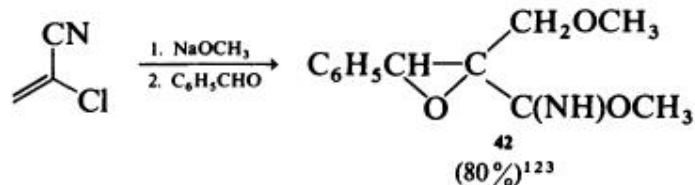
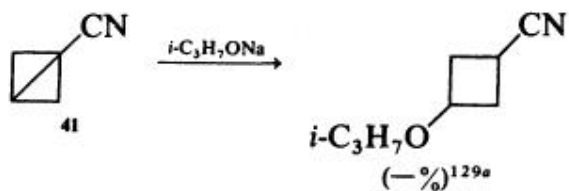
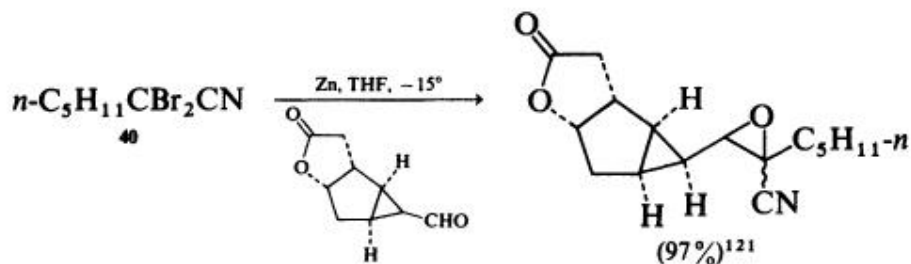
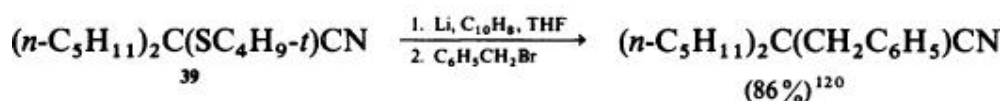
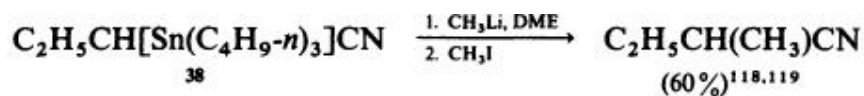


Vicinal dianions and distal dianions of mononitriles obviously require a second stabilizing group (or groups) to obtain the polymetalated species. In the case of vicinal dianions, (108-110) the introduction of β -phenyl groups in a propionitrile provides the expected stabilization and allows the preparation of the dipotassium salt of 2,3,3-triphenylpropionitrile (29). (110) As expected, the most nucleophilic site in such vicinal dianions corresponds to the carbon in the starting material bearing the least acidic hydrogen. Consonant with this expectation, the monoalkylation of the dianion 30 furnishes the β -alkylated nitrile 31, (110) whereas the monoalkylation of the monoanion 32 (110) provides the isomeric product 33. Additional examples involving the regioselective alkylation of dianions include the alkylation of β -cyanoketones such as 34, which provides a synthetic pathway for the β -alkylation of enones. (111) Finally, trapping both nucleophilic centers in vicinal dianions with a bifunctional electrophile leads



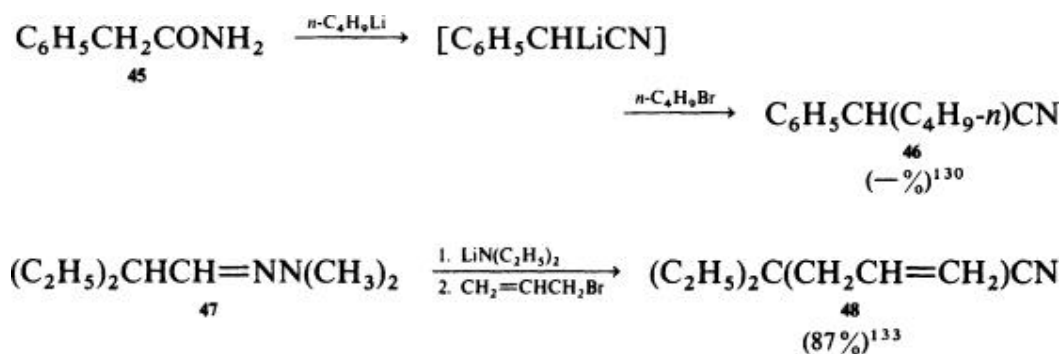
2.1.1.3. Alternative Methods for Generating Nitrile Anions

Although deprotonation constitutes the most widely practiced method for generating nitrile anions, several synthetically useful alternatives exist for their generation from nitrile as well as nonnitrile precursors. The methods that start with nitrile-containing materials include the electrochemical generation of nitrile anions, (113, 114) chemical reduction (115) of α , β -unsaturated nitriles, transmetalation of α -(trialkylstannyl)nitriles, (116-119) reduction of α -thioalkoxynitriles (120) or α , α -dibromonitriles, (121) and conjugate addition of nucleophiles to either α , β -unsaturated nitriles (122-127) or cyclopropanecarbonitriles. (128, 129) The scope of these alternatives varies considerably. Those procedures involving the transmetalation of α -(trialkylstannyl)nitriles such as **38** (118, 119) or the reduction of α -thioalkoxynitriles or α , α -dibromonitriles such as **39** (120) and **40**, (121) respectively, reach objectives that are accessible by direct alkylation procedures from simpler starting materials. The example involving the addition of sodium isopropoxide to 1-bicyclobutanecarbonitrile (**41**) (129) is also an interesting but synthetically limited reaction. Those reactions illustrated by the tandem conjugate addition and alkylation of either acrylonitrile or α -chloroacrylonitrile offer considerable synthetic promise in providing relatively complex products **42**, **43**, and **44** from simple starting materials in a single step.



Several interesting routes to nitrile anions employ fragmentation reactions of precursors that do not originally contain nitrile functionality. The elimination of lithium oxide from the trilithiated derivative of phenylacetamide (45) constitutes an unusual synthesis of the phenylacetone nitrile anion (130, 131) and furnishes a

synthesis of monoalkylated phenylacetonitrile derivatives as illustrated by the preparation of 2-phenylhexanenitrile (**46**). (130) The requirement for *n*-butyllithium for generation of the trilithiated amide intermediate limits the scope of this method. Another procedure involves the fragmentation of *N,N*-dimethylhydrazones using lithium diethylamide to obtain nitrile anions that are subsequently alkylated by halides, carbonyl compounds, and epoxides. (132, 133) This method is successful for those hydrazones branched at the α -carbon as illustrated for the conversion of the hydrazone **47** to the alkylated nitrile **48**. (133) Hydrazones derived from straight-chain aldehydes undergo preferential metalation at the α -carbon (132) rather than the sp^2 -hybridized imine carbon.



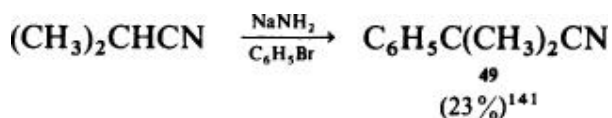
2.2. Influence of Electrophile

Nucleophilic substitution and addition reactions of nitrile-stabilized carbanions embrace a variety of mechanisms depending on the nature of the electrophilic partner. A thorough discussion of these mechanistic possibilities is clearly beyond the scope of this chapter, but a brief presentation highlights the significant differences encountered with different electrophiles in their reactions with arylacetonitriles and alkylacetonitriles. The reader is referred to several authoritative reviews of carbanion chemistry, (134-136) for a detailed discussion of mechanism. Since the reactions of nitriles bearing α -oriented oxygen, sulfur, selenium, nitrogen, or halogen functionality generally parallel the reactions of simple nitriles, these reactions are not discussed in any detail.

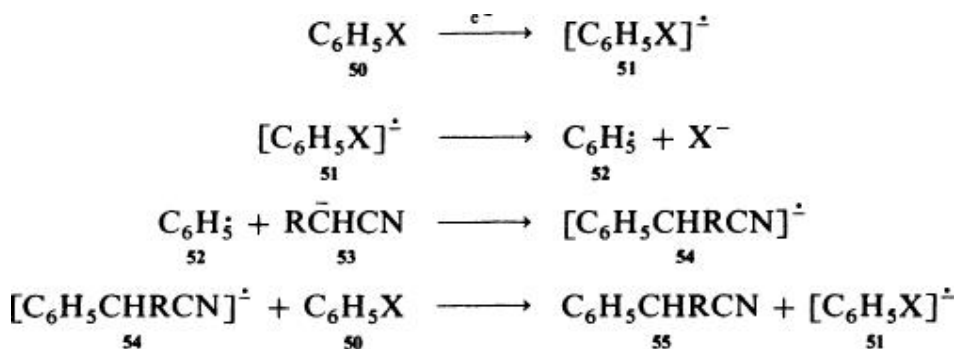
Available evidence (1) indicates that the alkylation of nitrile anions follows a bimolecular nucleophilic (S_N2) mechanism. As a consequence, the range of alkylating agents that react with nitrile anions, the stereochemical outcome expected for such reactions, and the influence of solvent (137, 138) reflect similar patterns seen for other S_N2 reactions. The reader is referred to an earlier chapter in this series (1) that deals extensively with such aspects of nitrile alkylations and provides specific evidence to support these assertions. An electron-transfer mechanism accounts for alkylations of nitriles with tertiary

alkyl halides. (139)

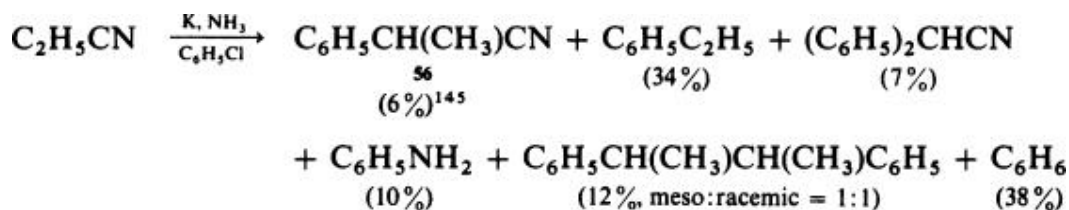
The arylation of nitrile anions involves an array of different mechanisms depending on substrate structure and reaction conditions. An elimination–addition sequence involving benzyne intermediates (140) accounts for substitution reactions of aryl halides lacking electron-withdrawing groups. Specific reactions of benzyne intermediates with nitrile-stabilized anions such as the conversion of isobutyronitrile to the nitrile **49** (141) has received only scattered attention, (141-143) and the mechanism for these substitutions is assigned by analogy to other well-precedented carbanion additions to benzyne. Reactions involving substituted aryl halides that might exhibit *cine* substitution have not been investigated.



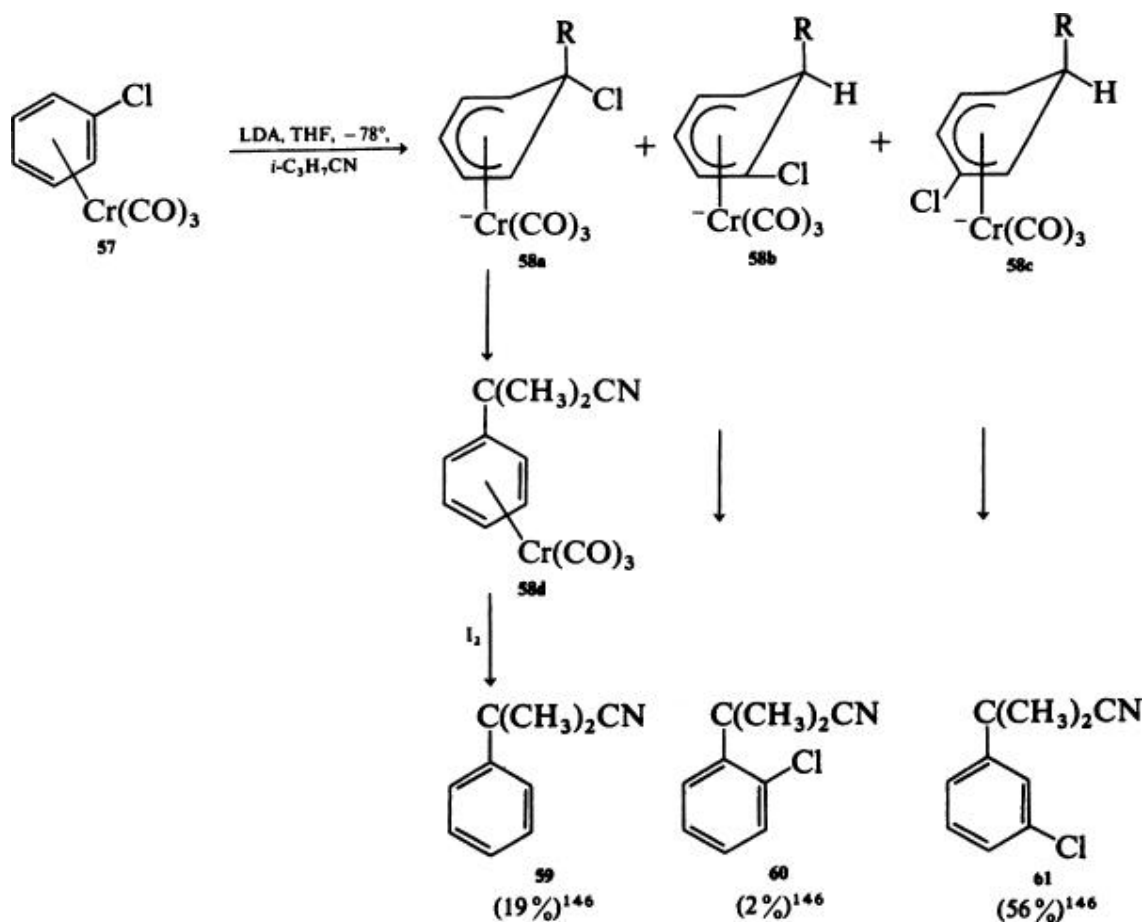
Identification of the radical-chain mechanism ($S_{RN}1$) for aromatic nucleophilic substitution (144, 145) opens a new approach for effecting regiospecific substitution in unactivated aryl halides, aryl phosphates, and aryl (trialkyl)-ammonium halides by various nucleophiles, including nitrile-stabilized carbanions. Initial electron transfer supplied by an alkali metal to the aryl substrate **50** in ammonia produces the radical anion **51**. In addition, irradiation of enolate anions and aryl halides also induces the generation of the appropriate radical anion **51** in a photostimulated version of the $S_{RN}1$ reaction. In subsequent steps, fragmentation of the radical anion **51** furnishes the aryl radical **52** that combines with the nucleophile **53** to form a new radical anion **54**. Electron transfer from **54** to a second aryl substrate **50** furnishes the substitution product **55** and propagates a chain reaction by regenerating the radical anion **51**.



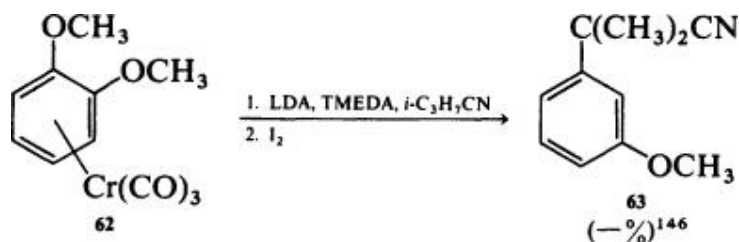
In those cases involving nitrile-stabilized carbanions, nucleophilic substitution by the $S_{RN}1$ mechanism is accompanied by numerous side reactions. (145) For example, the reaction of nitriles with various halobenzenes using potassium metal in liquid ammonia affords several products as illustrated by the reaction of propionitrile with chlorobenzene. (145) The poor yield of 2-phenylpropionitrile (56) results from the proclivity of the anion radical progenitor of 56 to lose cyanide ion. This fragmentation generates a benzyl radical that undergoes either further reduction or dimerization. Photostimulated phenylations of nitrile-stabilized anions encounter the same difficulties. In the present stage of development, the $S_{RN}1$ reactions are inferior to the classical $S_{N}Ar$ reactions as a preparative route to simple, substituted arylacetonitriles.



The activating influence of a metal center on the reactivity of aromatic rings finds application in the reactions of arene chromium tricarbonyl complexes with nitrile-stabilized anions. (146) Evidence consistent with the intermediacy of π -(alkylcyclohexadienyl)chromium tricarbonyl anions includes direct NMR evidence as well as product analysis from experiments quenched with various electrophiles. (147) In the case of (π -chlorobenzene)chromium tricarbonyl (57) and the anion of isobutyronitrile, a rapid equilibrium is established in which attack occurs at several positions on the aromatic ring. In the nitrile anion adducts, complex 58a undergoes a relatively slow elimination of chloride to give a π -(alkylbenzene)chromium tricarbonyl 58d. Oxidative removal of the metal species from the intermediates 58b, 58c, and 58d accounts for the observed

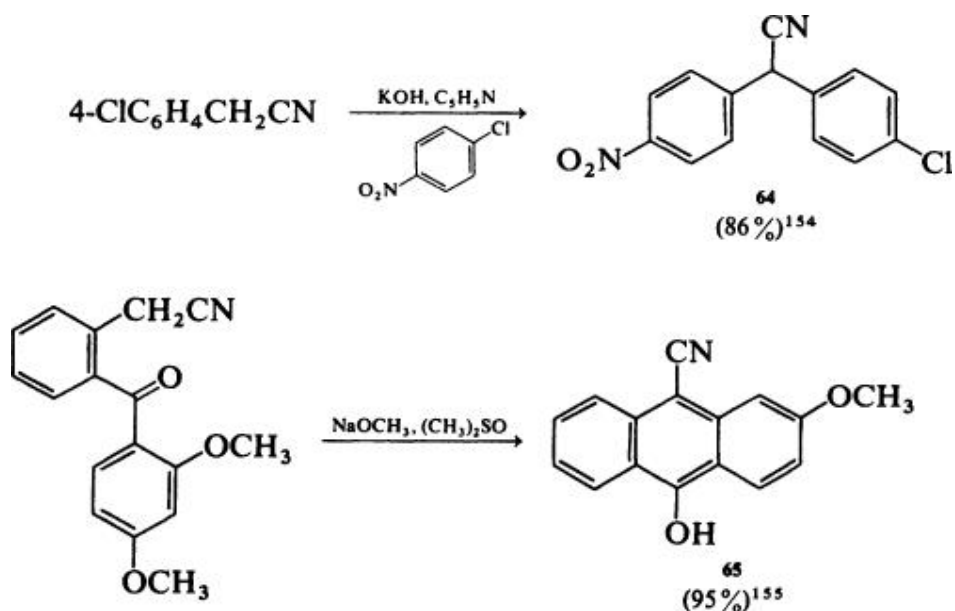


products. One exception to this mechanistic picture involves the *cine* substitution observed in the conversion of the *ortho*-disubstituted complex **62** to the *meta*-disubstituted product **63**. The outcome in this case was attributed to an intermediate aryne complex, although direct evidence for this pathway is not available. (146)

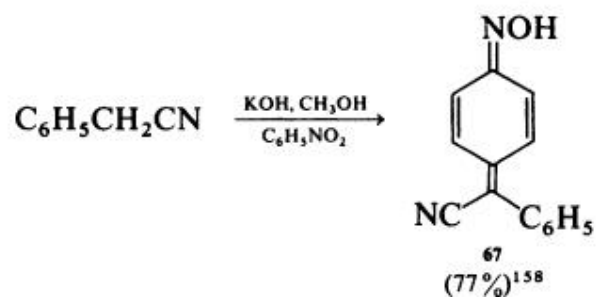
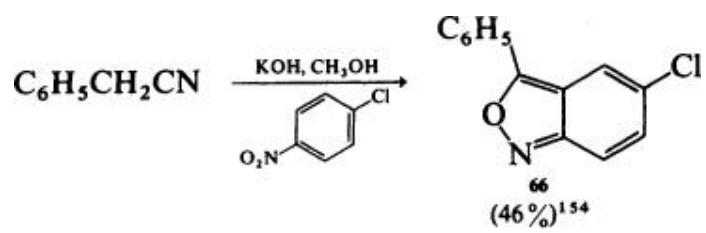


In cases where the aromatic electrophile bears both electron-withdrawing groups and a potential leaving group, an addition-elimination ($\text{S}_{\text{N}}\text{Ar}$) mechanism operates to produce the usual cyclohexadienyl anion that subsequently expels the leaving group. (148-153) In the particular case where

nitrile-stabilized anions act as nucleophiles, this key intermediate cascades to a variety of products depending principally on the structure of the electrophile. Both intramolecular and intermolecular examples of the traditional S_NAr mechanism exist for nitroaromatic substrates where chloro, methoxy, and nitro groups are leaving groups. The preparation of the substituted diphenylacetonitrile **64** (154) and the cyanoanthrol **65** (155) illustrate these reactions. Somewhat more unusual cases derive from nucleophilic attack at carbons not bearing a traditional leaving group. Attack of nitrile-stabilized anions on the unsubstituted *ortho* position of



nitroaromatics leads to benzoxazoles (154, 156) such as **66**, and on the unsubstituted *para* position of nitroaromatics such attack yields *p*-quinonemethide oximes (157, 158) such as **67**.

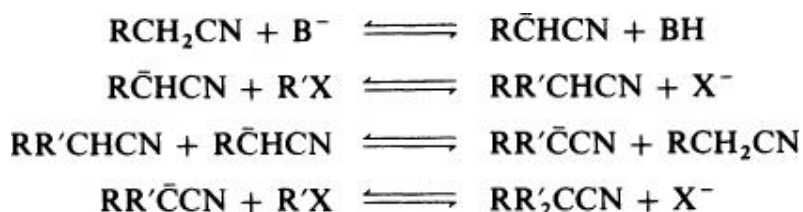


3. Scope and Limitations

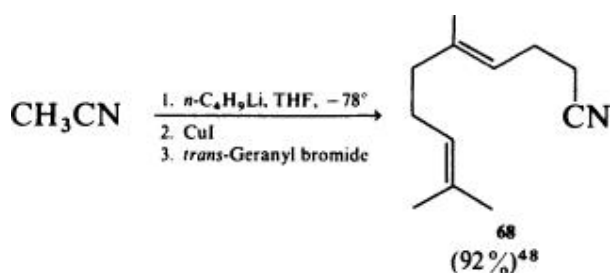
3.1. Reactions of Nitrile-Stabilized Carbanions

3.1.1.1. Alkylation

All procedures designed to effect the monoalkylation of primary nitriles must contend with formation of dialkylated product. The basis for this competing reaction resides in the equilibria between the monoalkylated product and either the anion of the starting material or the base. In cases where molar equivalents of base and alkylating agent are employed, the synthesis of dialkylated product is accompanied by an equivalent amount of unalkylated material.

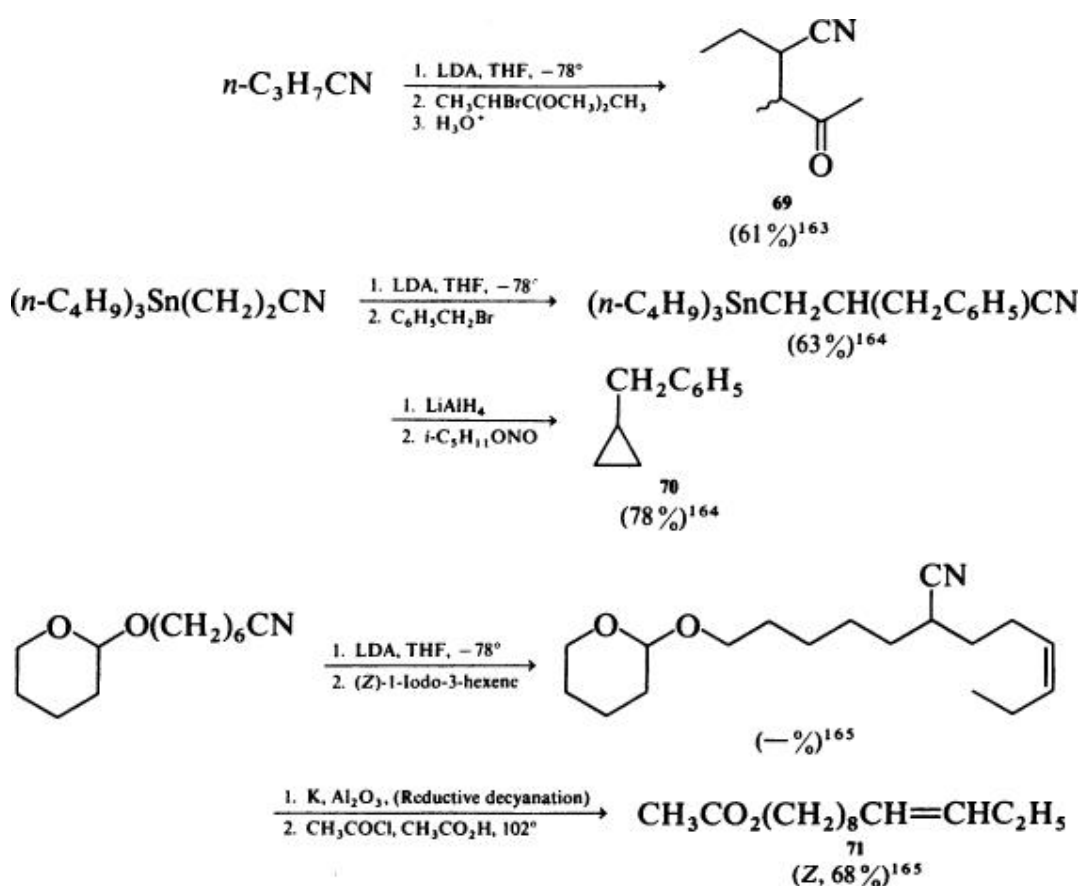


The alkylation of acetonitrile itself presents an interesting problem in that mono-, di-, and trialkylation reactions are all possible. Not unexpectedly, few studies have focused on interrupting the polyalkylation of acetonitrile to obtain mono- or dialkylated products, and in those studies that are available, the yields are invariably low as a survey of the tables would indicate. Exceptions to this statement include reactions of lithioacetonitrile with epoxides where the negatively charged alkoxide intermediate suppresses a subsequent deprotonation at the α position of the nitrile adduct. (159, 160) The utilization of a cyanomethylcopper(I) species also proves advantageous in the monoalkylation of acetonitrile with various allylic halides such as *trans*-geranyl bromide to give the nitrile **68**. (48)



Successful monoalkylations of primary nitriles employ strong bases such as

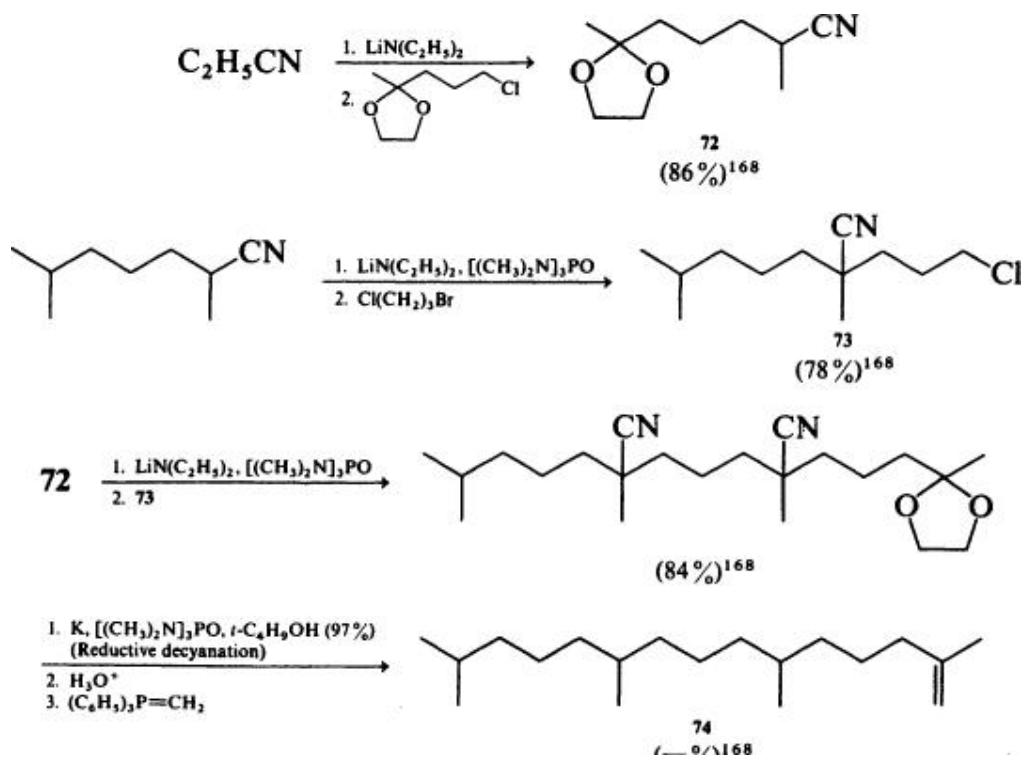
alkali metal hydrides, amides, dialkylamides, or bis(trimethylsilyl)amides to generate high concentrations of the requisite nitrile anions and use reactive primary or secondary alkyl halides or sulfonates to intercept the nitrile anions. Exceptions to this generalization include the successful monoalkylations of arylacetonitriles using sodium hydroxide under phase-transfer conditions. Best yields of monoalkylated products are often encountered with the use of secondary rather than primary halides, where further alkylation is minimized by the steric interactions between the anion of the monoalkylated product and a second alkyl halide. (161, 162) Several interesting applications illustrating such monoalkylations of primary nitriles include the preparation of the β -cyanoketone **69**, (163) benzylcyclopropane (**70**), (164) and the sex pheromone **71** of *Pazalobesia viteana*. (165)

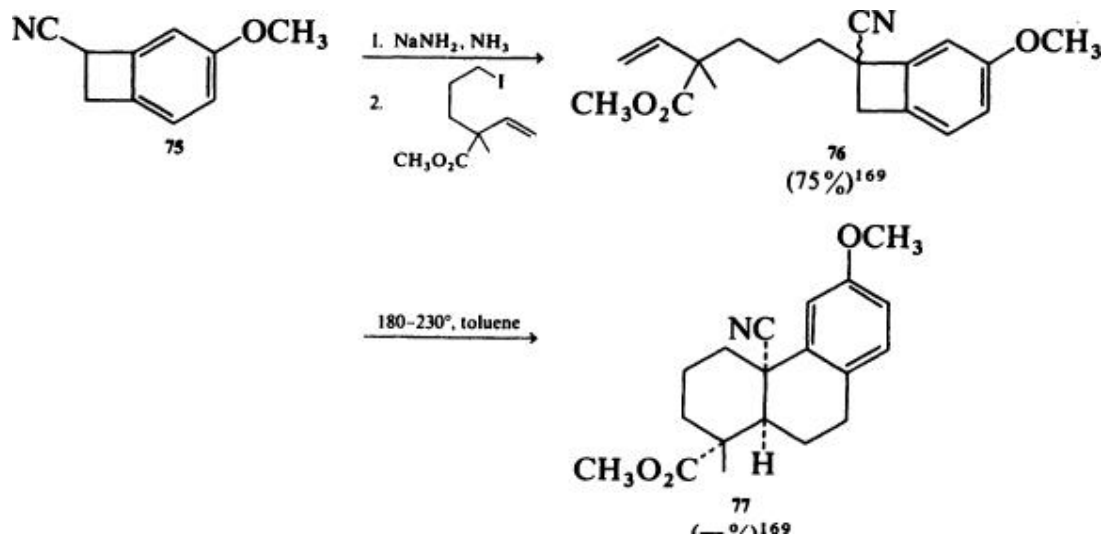


Alkylation of secondary nitriles obviously involves fewer problems than the alkylation of primary nitriles, although the same conditions are generally employed for either family. In detailed studies using 2-phenylpropionitrile, the yields of monoalkylated product are independent of the halide, (166) although one report indicates that alkyl iodides are less satisfactory than other alkyl

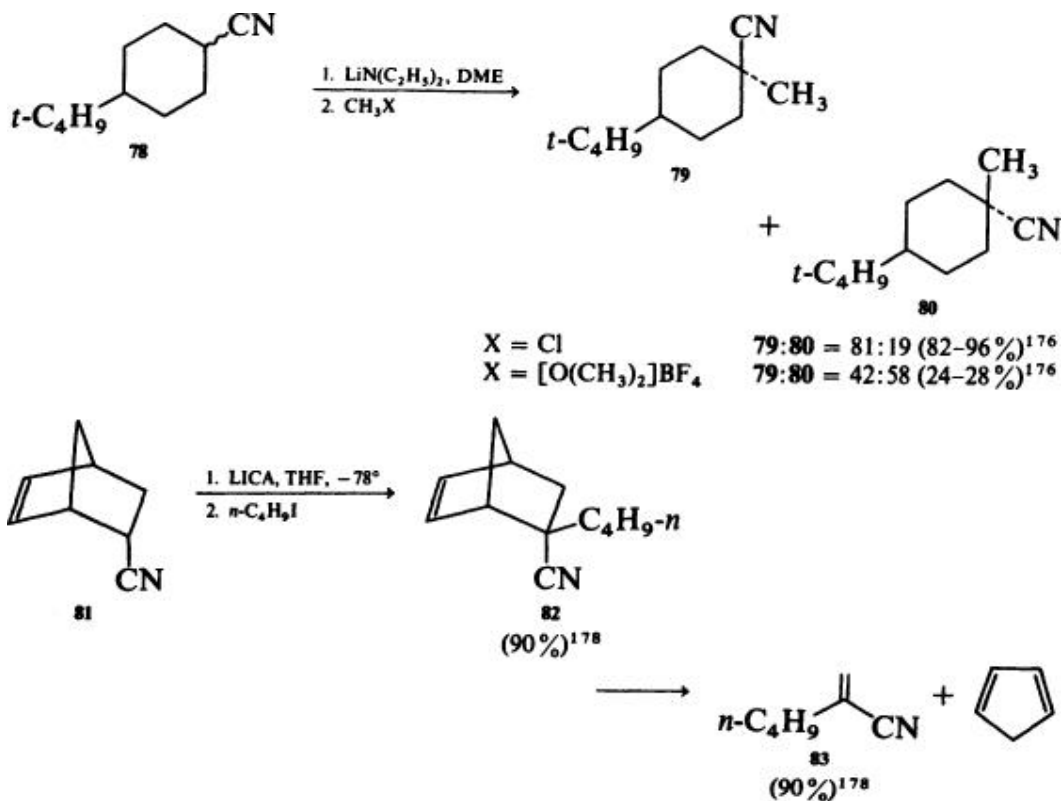
halides. (167) The yields of alkylated product from the reactions of 2-phenylpropionitrile with various isomeric butyl chlorides (166) using sodium amide in toluene decrease in the order: $i\text{-C}_4\text{H}_9 > \text{sec-C}_4\text{H}_9 > n\text{-C}_4\text{H}_9 \geq t\text{-C}_4\text{H}_9$. Yields of alkylation products of the same nitrile with various isomeric pentyl chlorides (167) decline in the same order. In the reactions of 2-phenylbutyronitrile with various isomeric butyl chlorides, (42) yields fall in the order: $\text{sec-C}_4\text{H}_9 > i\text{-C}_4\text{H}_9 > n\text{-C}_4\text{H}_9 \geq t\text{-C}_4\text{H}_9$. A report that the direct alkylation of 2,3-diphenylpropionitrile to give 2-methyl-2,3-diphenylpropionitrile requires only methylmagnesium iodide (51) is probably in error. Unreacted methyl iodide in conjunction with the Grignard reagent functioning as the base probably accounts for the observed result. Applications of such alkylations include a synthesis of norphytene (74) (168) by successive nitrile alkylations and reductive decyanation as well as syntheses of steroids and diterpenes. (169-175) In an approach to diterpene alkaloids, the alkylation of the nitrile 75 furnishes the adduct 76 (169) in which the benzocyclobutene represents a masked diene. Pyrolysis of 76 liberates the σ -quinodimethane that undergoes a regioselective, intramolecular Diels–Alder reaction to give the tricyclic intermediate 77. (169)

The stereochemical preferences for the introduction of an alkyl group have been examined in reactions of certain cyclic, secondary nitriles. In reactions of





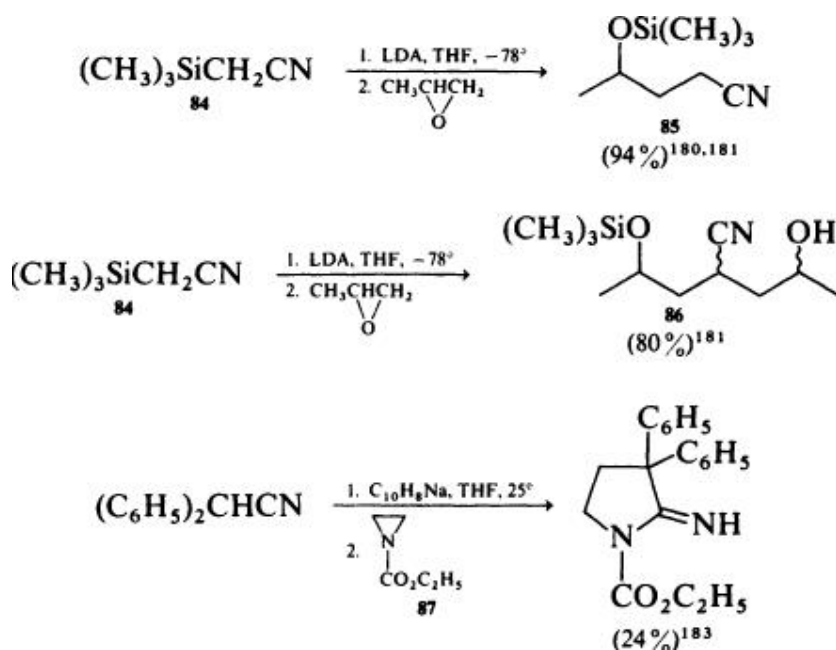
the stereochemically anchored 4-*tert*-butylcyclohexanecarbonitrile (**78**), the ratio of equatorial to axial methylation varies from 81 : 19 for methyl chloride to 42 : 58 for trimethyloxonium tetrafluoroborate. (176) This pattern is consistent with a reactant-like transition state in which the less reactive methyl chloride involves a greater degree of bonding with the nucleophile and hence exhibits a greater degree of stereodiscrimination than the reactive trimethyloxonium tetrafluoroborate. Alkylation of 5-norbornene-2-carbonitrile (**81**) gives the *exo*-alkylated product **82** preferentially and provides a synthetic route to various α -substituted acrylonitriles **83** (177, 178) by a retro-Diels–Alder reaction.



The dialkylation of primary nitriles is valuable in reactions where both alkyl groups to be introduced are identical or where α , ω -dihaloalkanes are used as the electrophilic partners. The former case is relatively unexceptional, although in the case of sodium amide, it is interesting that a successful dialkylation experiment depends critically on the excess alkylating agent consuming the excess sodium amide. (162) Use of four equivalents each of sodium amide and 1-bromo-butane to alkylate phenylacetonitrile furnishes the dialkylated product in 92% yield; an excess of sodium amide without the excess of alkyl halide converts the dialkylated product to its amidine derivative. This problem is also circumvented by employing hindered lithium dialkylamides rather than sodium amide as bases.

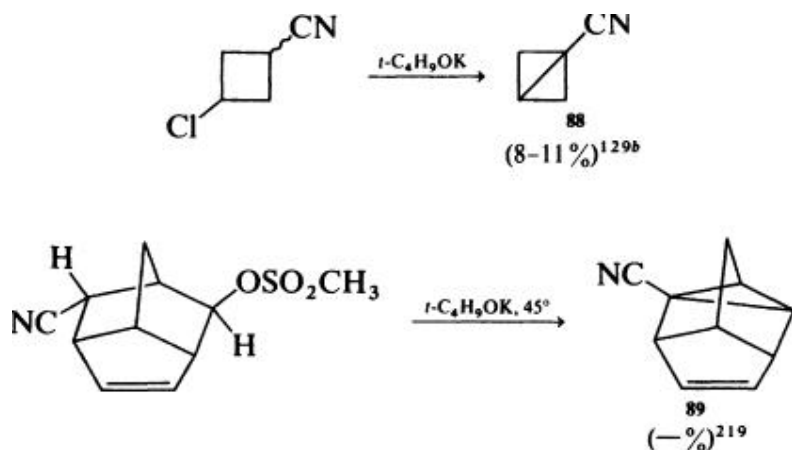
Epoxides serve as useful electrophilic partners in reactions with nitrile anions (159, 160, 179, 180) to give γ -hydroxynitriles. An interesting variant of this reaction involves the use of trimethylsilylacetonitrile (84) (181) to afford the trimethylsilylated product 85 through intramolecular silyl group migration. An excess of the epoxide component in this latter reaction leads to the bisadduct 86 in which the two hydroxyl groups are differentiated. The utility of γ -hydroxynitriles is illustrated by their conversion to γ -lactones (181, 182) and 1,4-diketones. (180) Only a limited number of cases employing aziridine

electrophiles such as **87** have been reported, (183) although aziridinium salts presumably serve as electrophiles in the aminoalkylation of nitriles.

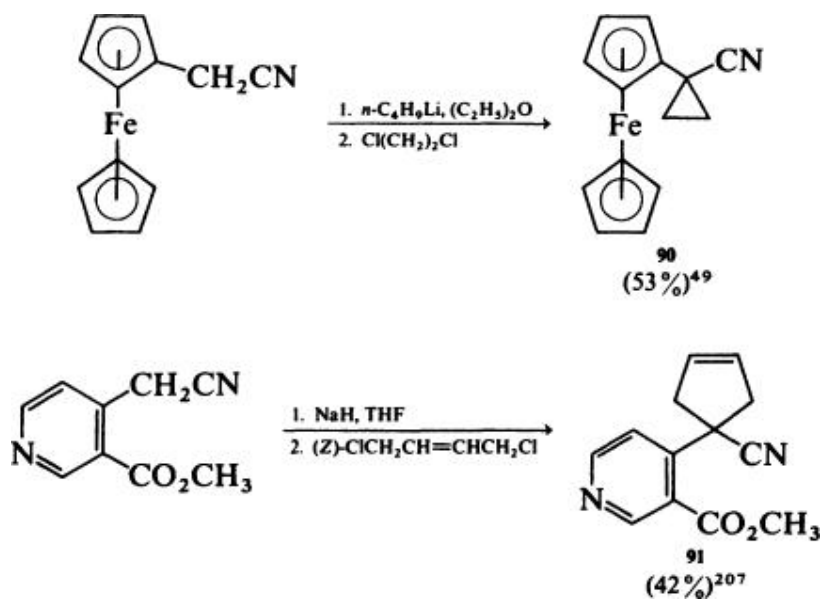


3.1.1.2. Cycloalkylation

The alkylation of a primary nitrile with an α, ω -dihalide involves an intramolecular reaction of an ω -halonitrile as the second step in a general synthesis of cycloalkanecarbonitriles. This approach has been applied to the synthesis of cyclopropanes, (46, 47, 49, 97, 102, 107, 184-190) cyclobutanes, (47, 97, 105, 190-193) oxetanes, (194) cyclopentanes, (47, 70, 71, 80, 85, 97, 105, 191, 195-207) cyclohexanes, (70, 97, 105, 191, 199, 201, 202, 204, 206, 208-210) tetrahydropyrans, (70, 201, 202) tetrahydrothiopyrans, (211) piperidines, (212-217) and cycloheptanes, (105, 193) as well as unusual silicon-containing heterocycles. (218) Leaving groups other than halides such as mesylates, (219) epoxides, (220-225) and sulfonium salts (52) also suffice. The approach is sufficiently general to provide avenues to an array of polycyclic systems as illustrated by the syntheses of strained ring systems in nitriles **88** (226) and **89**. (219)

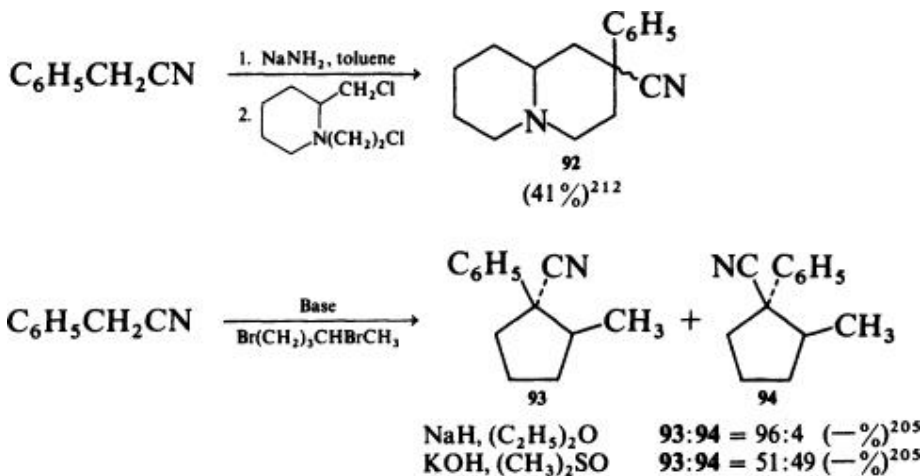


The most common intramolecular alkylations involve the second step in the dialkylation of a primary nitrile with a symmetrical α, ω -dihalide as illustrated by the preparation of cyclopropane **90** (49) and cyclopentene **91**. (207) Unsymmetrical α, ω -dihaloalkanes in which the halogens either differ or exist in different environments also undergo dialkylation with primary nitriles to give

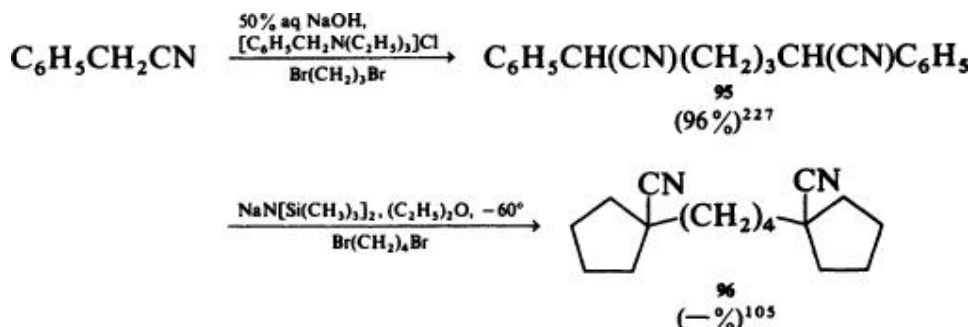


useful products as in the preparation of **92**. (212) In this case, the usual order of leaving-group ability for halides or rates of S_N2 substitution at primary versus secondary centers dictates the structure of the intermediate monoalkylated adduct. The stereochemical outcome in the second, intramolecular step varies as a function of the substituents on the interacting centers as well as the reaction conditions. These factors are illustrated for the

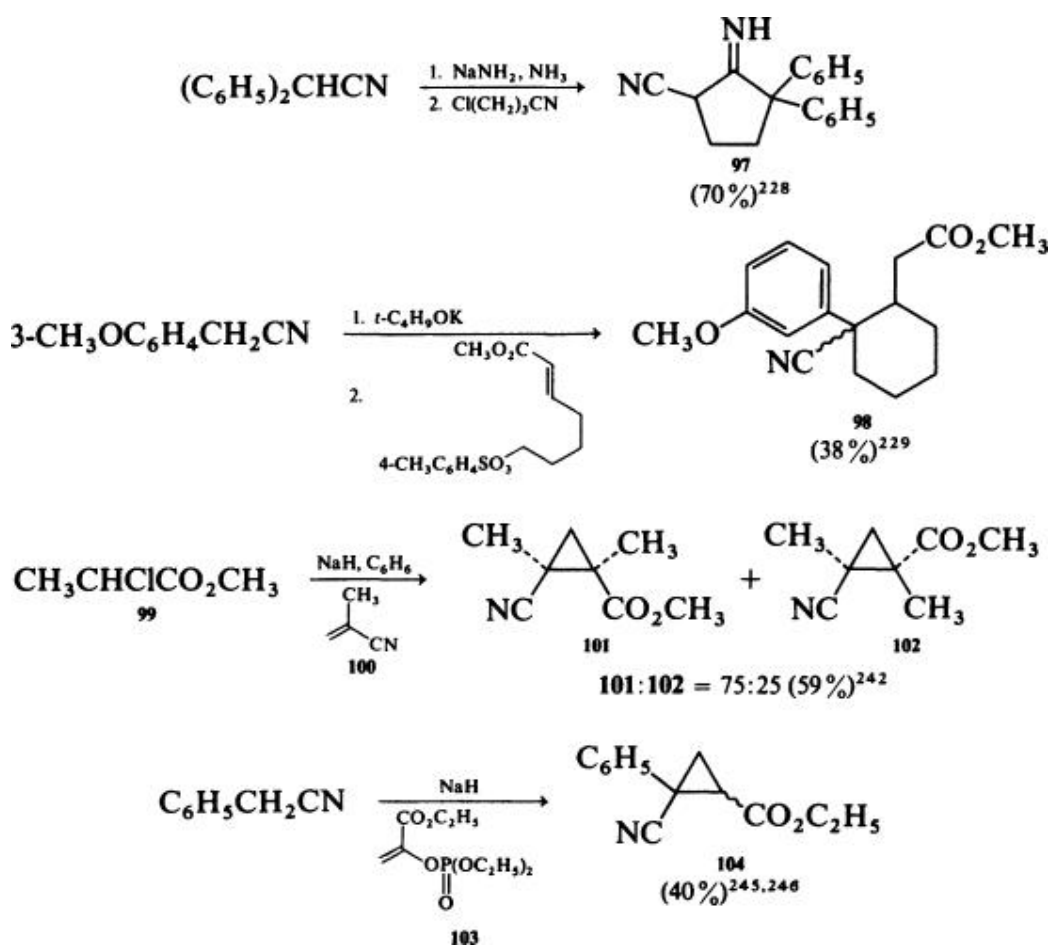
alkylation of phenylacetonitrile with 1,4-dibromopentane to give the cyclopentanes **93** and **94**. (205)



As a group, the cycloalkylation reactions deal largely with primary arylacetonitriles for which the following bases are most commonly employed : sodium amide, (102, 184, 186, 190-192, 195, 196, 211-213) lithium amide, (188, 189) sodium hydroxide under phase-transfer conditions, (70, 71, 80, 85, 97, 201, 202, 214, 215) *n*-butyllithium, (46, 47, 49, 102) and sodium hydride. (207, 216, 217) Less commonly used bases include sodium hydroxide, (197, 199, 200) potassium hydroxide, (203) sodium naphthalide, (198) potassium *tert*-butoxide, (208, 210) sodium methylsulfinylmethide, (204) and lithium diisopropylamide. (107) For unsaturated and saturated aliphatic nitriles, the most common bases are sodium bis(trimethylsilyl)amide, (105, 226) sodium hydride, (187) sodium amide, (209) and lithium dialkylamides. (193, 206) The side reactions encountered in the cycloalkylation of primary nitriles involve competitive intermolecular condensations as illustrated by the formation of the bisnitrile **95** (227) in the alkylation of phenylacetonitrile or, in the special case of acetonitrile, the intermolecular alkylation of the cyclic product with another α , ω -dihaloalkane to give the bicyclic dinitrile **96**. (105)

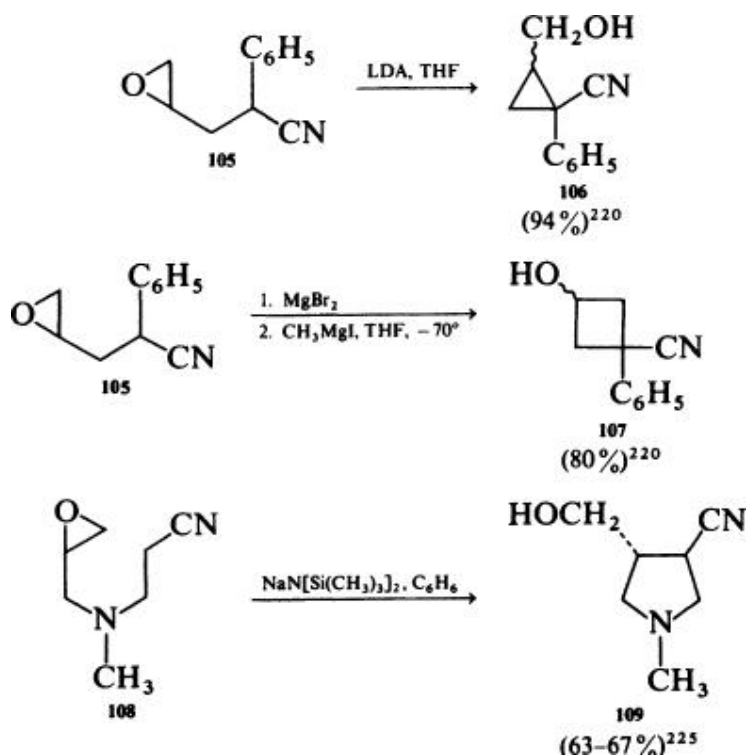


The cycloalkylation of nitriles need not involve just dialkylation reactions. Several interesting ring-forming reactions involve a combination of alkylation and addition reactions. The synthesis of the α -cyanoimine **97** (228) and the cyclo-hexanecarbonitrile **98** (229) illustrates alkylation reactions in tandem with addition reactions to a nitrile or unsaturated ester, respectively. Other examples include the addition of the anions of α -chloroesters to substituted acrylates or acrylonitriles to furnish cyclopropanes (230-244) as shown in the condensation of methyl 2-chloropropionate (**99**) to methacrylonitrile (**100**). (242) Alternatively, an example where the Michael acceptor also bears the leaving group involves the reaction of phenylacetonitrile and ethyl diethylphosphoenolpyruvate (**103**) to give the cyclopropane **104**. (245-247) Deuterium labeling studies show the operation of an intramolecular 1,3-proton shift prior to the cyclization that gives the cyclopropane **104**. (247)

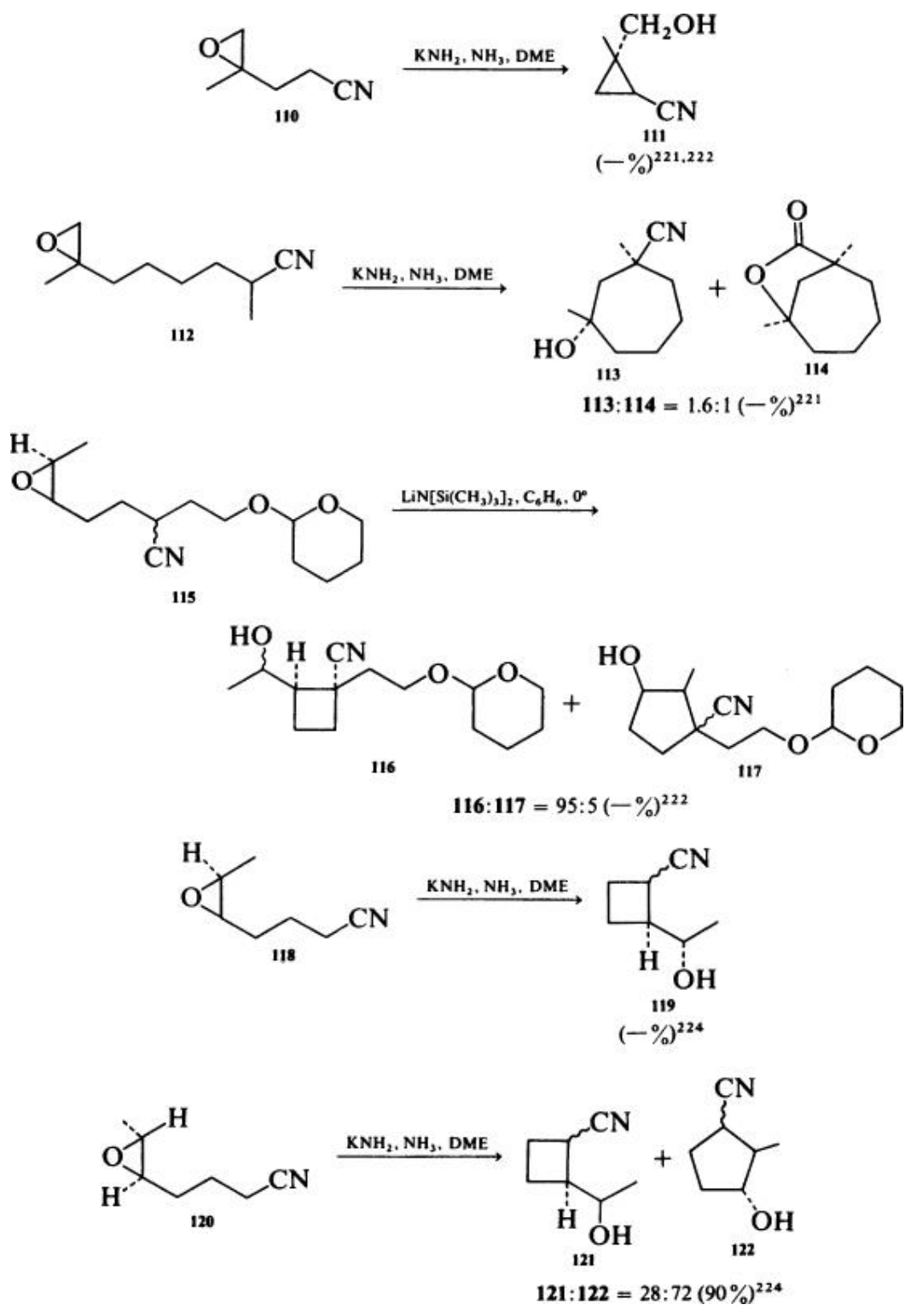


The cyclization of ω -epoxynitriles offers several unique synthetic advantages. In cases where the carbon chain connecting the epoxide and nitrile groups is relatively short, only the highly nucleophilic carbon and not the nitrogen of the ambident nitrile anion can participate in the cyclization. Although the epoxide group in such ω -epoxynitriles appears to offer two potential sites for intra-molecular cyclization, distinct regiochemical preferences make these cyclizations synthetically useful. This regioselectivity reflects the requirement for a collinear arrangement of the nucleophile and the leaving group in the transition state for the cyclization. (221-223, 248) Superimposed on this preference is the fact that nucleophilic attack on unsymmetrical epoxides usually occurs at the least-substituted carbon.

For ω -epoxynitriles bearing a monosubstituted epoxide separated by two to four intervening atoms, ring-forming reactions involving attack at the most substituted internal carbon of the epoxide are favored relative to attack at the terminal carbon. This outcome reflects the dominant influence of the collinearity principle; consequently, the epoxynitrile **105** undergoes cyclization to give the cyclopropane **106**. (220) This regiochemical result is reversed when the epoxynitrile **105** is treated with methylmagnesium iodide, but in this case, opening of the epoxide to the iodohydrin precedes cyclization to the cyclobutane **107**. (220) A heterocyclic variant of this reaction involving the epoxynitrile **108** proceeds to give the pyrrolidine **109**. (225)

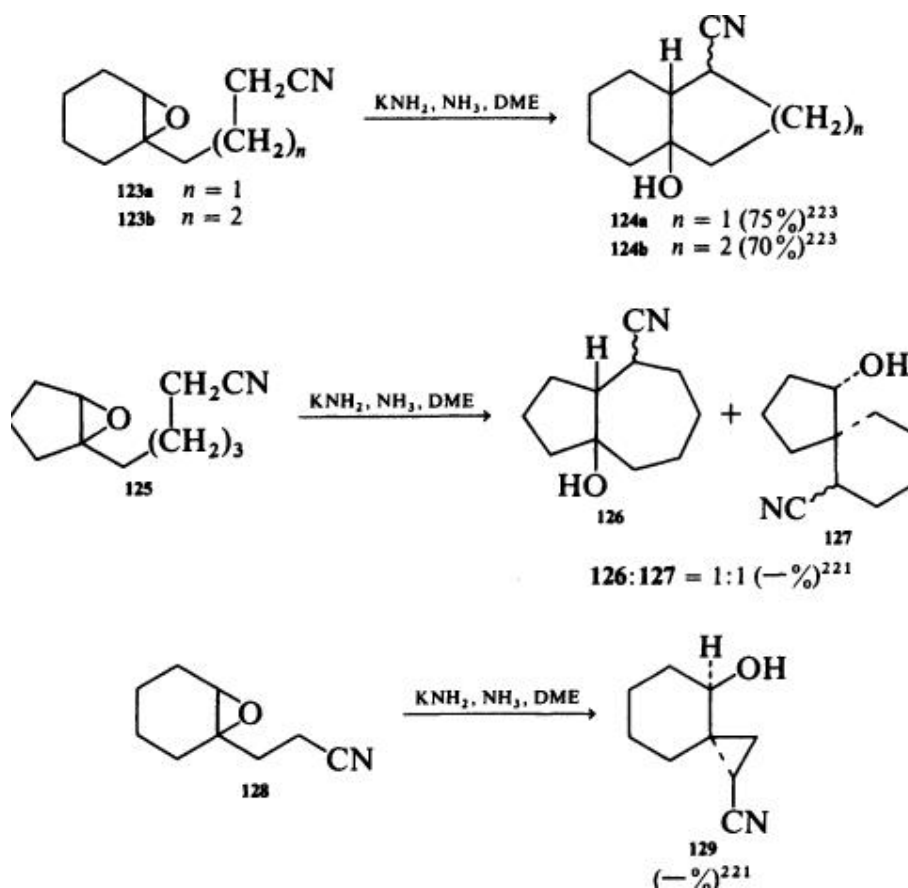


The cyclization of ω -epoxynitriles bearing 1,1-disubstituted epoxides also follows the collinearity principle as illustrated by the cyclization of epoxynitriles **110** and **112**. (221, 222) The former reaction again shows that this collinear arrangement of reacting centers overrides the usual considerations of nucleophilic attack on the least-substituted carbon of the epoxide. The cyclization of ω -epoxynitriles bearing 1,2-disubstituted epoxides is complicated by the influence of epoxide stereochemistry. For 1,2-*cis*-epoxides such as **115** (222) and **118**, (224) cyclization favors the smaller ring leading to the predominant formation of cyclobutanes **116** and **119**, respectively, rather than cyclopentanes. The stereochemistry of **118** is not specified, (222) but the use of a Wittig reaction to prepare the 5-heptenenitrile precursor to **118** suggests that the *cis* isomer is the correct structure for the starting material. For ω -epoxynitriles bearing 1,2-*trans*-epoxides, the cyclization leads to the larger ring as illustrated by the preference for the cyclopentane **122** rather than the cyclobutane **121** in the cyclization of **120**. (224)

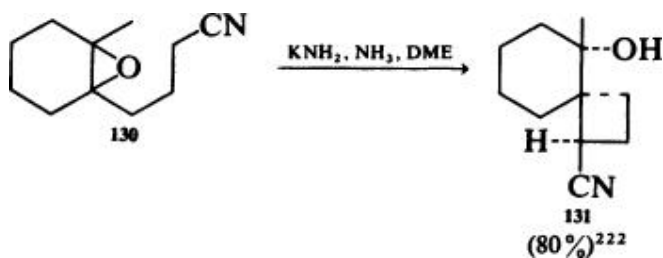


A preference for S_N2 attack at the least-substituted carbon of an epoxide governs the cyclization of ω -epoxynitriles bearing trisubstituted epoxides.

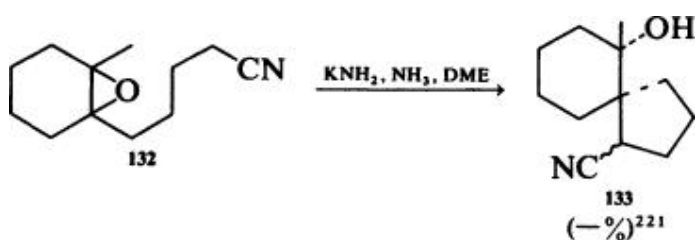
Consistent with this generalization, cyclization of the ω -epoxynitriles **123a** and **123b** leads to the *cis*-fused indane **124a** (223) and decalin **124b**, (223) respectively. In cases where six- and seven-membered ring cyclizations compete as in **125**, the fused ring product **126** and spirocyclic product **127** are formed in equal amounts. (221) The only exception to the usual preference for attack at the least-substituted end of the epoxide involves the cyclization of **128** to the cyclo-propane **129**, where the collinearity principle dictates the outcome observed.



For tetrasubstituted epoxides in ω -epoxynitriles, the cyclization proceeds to give the smaller ring. An illustration of this process involves the formation of the spirocyclic products **131** (222) and **133** (221) rather than fused-ring products in the



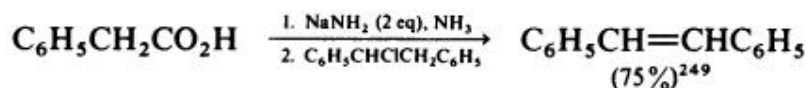
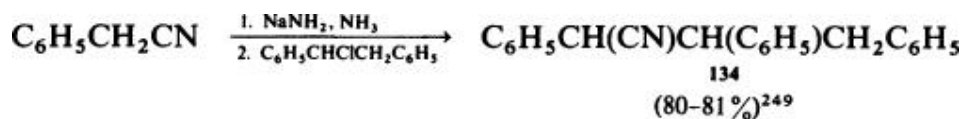
cyclization of ω -epoxynitriles **130** and **132**, respectively. Of particular interest is the stereospecific generation of three contiguous chiral centers in **133**, which holds great promise in the synthesis of natural products.



3.1.1.3. Side Reactions

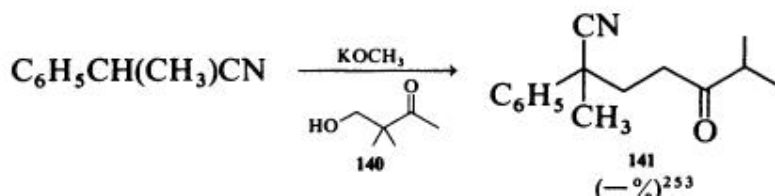
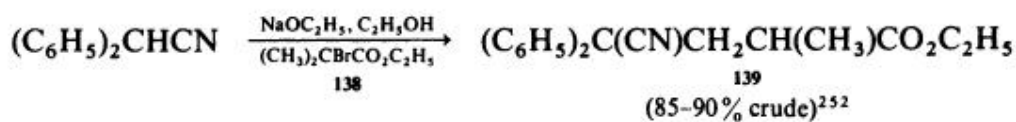
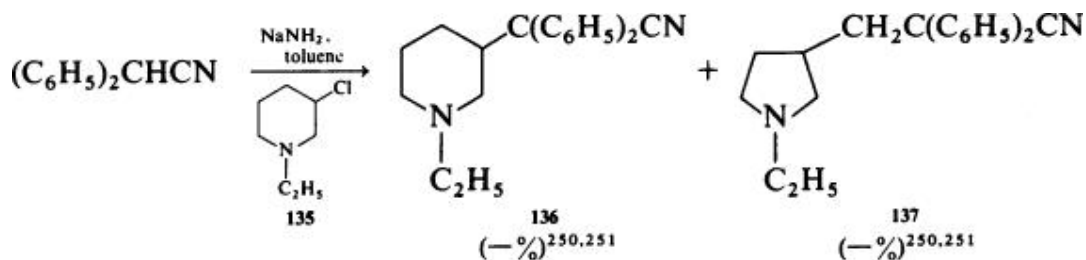
Apart from controlling the dialkylation problem during the monoalkylation of primary nitriles, several side reactions can intervene during the alkylation or acylation of nitriles. Fortunately, many of these side reactions can be avoided by selecting the appropriate experimental conditions. In a few instances, side reactions that were once considered as troublesome or as curiosities are now regarded as useful synthetic reactions.

Competitive side reactions that consume the alkyl halide involve dehydrohalogenation or substitution by nucleophilic bases. The use of hindered, nonnucleophilic bases such as lithium diisopropylamide or sodium bis(trimethylsilyl)amide circumvents this problem by generating high concentrations of the nitrile anion and generally innocuous amine byproducts. Dehydrohalogenation by nitrile anions themselves presents a problem in certain cases, although the successful alkylation by 1-chloro-1,2-diphenylethane of the anion of phenylacetonitrile to give the nitrile **134** should be contrasted with the exclusive elimination promoted by the dianion of phenylacetic acid to give stilbene. (249)



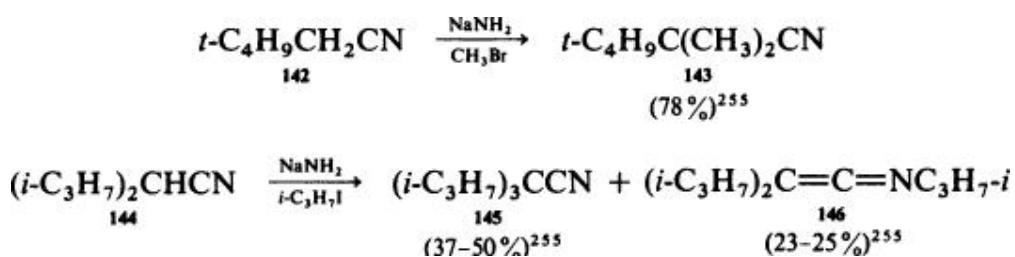
In certain instances, the consumption of excess base by alkyl halide actually protects the desired product from further alkylation. (162) In cases where an excess but equivalent amount of sodium amide and alkyl halide gives an excellent yield of alkylated product, the use of sodium amide:alkyl halide ratios greater than one leads to the amidine derived from the desired product.

Electrophilic reagents prone to undergo intramolecular or intermolecular reactions prior to alkylation often afford unexpected products. Acyclic or cyclic unsymmetrical 1-dialkylamino-2-haloethanes such as **135** furnish the alkylated products **136** and **137** through the alkylation of the intermediate aziridinium ion. (250, 251) Not unexpectedly, treatment of the α -bromoester **138** with the anion of diphenylacetonitrile leads to the product **139** derived from dehydrobromination and subsequent Michael addition. (252) Finally, the intervention of a retro-aldol–aldol condensation of the β -hydroxyketone **140** presumably accounts for the rearranged product **141**. (253)

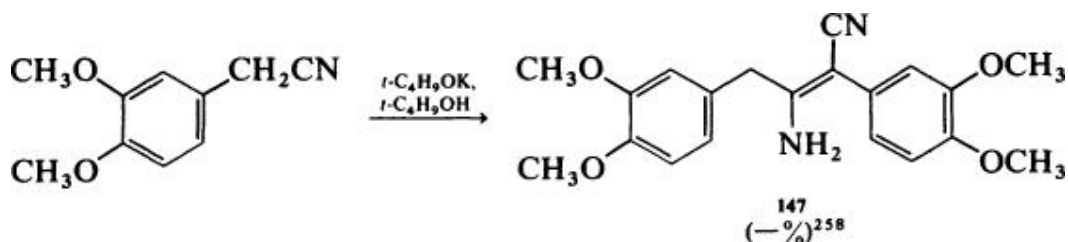


The ambident nitrile anion offers the potential for competitive *N*-alkylation in

addition to the desired C-alkylation. This process intervenes only in highly substituted systems, and Newman's "rule of six" (254) (i.e., the number of atoms that are six atoms from the nitrile nitrogen) correctly gauges those nitriles prone to give ketenimines. In general, those nitriles with a "six number" greater than or equal to 12 give ketenimines in addition to C-alkylated products. For example, 3,3-dimethylbutyronitrile (142) with a "six number" of 9 gives the C-alkylated product 143 (255) exclusively, whereas 2-isopropyl-3-methylbutyronitrile (144) with a "six number" of 12 gives a mixture of C-alkylated and N-alkylated products 145 and 146. (255) An increase in the number of carbon *versus* hydrogen substituents in the "six position" also increases the N-alkylation: C-alkylation ratio. (256)

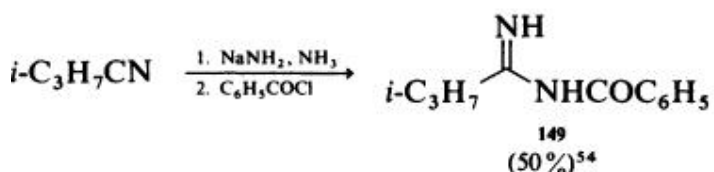
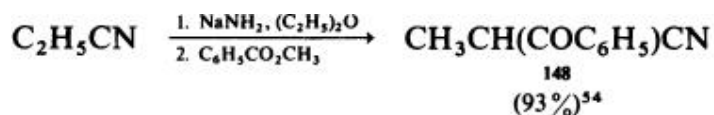


Other side reactions that affect the nitrile component in alkylation reactions arise from the condensation of the nitrile with bases or with another nitrile anion. The nitrile component is susceptible to self-condensation where the nitrile and nitrile anion coexist in solution. The intramolecular version of this reaction is, of course, well known as the Thorpe–Ziegler condensation. (257) In general, intermolecular condensations of this type leading to β -aminocrotonitriles (258, 259) such as 147 (258) result when alkoxide bases in protic media are used to generate the nitrile-stabilized carbanion.



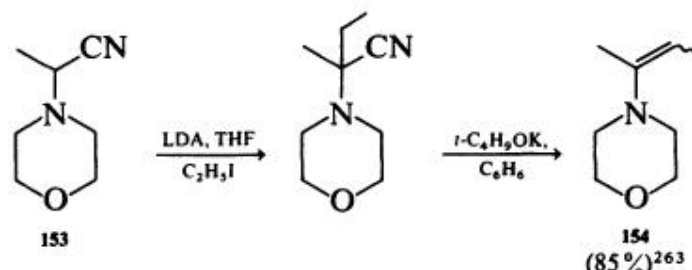
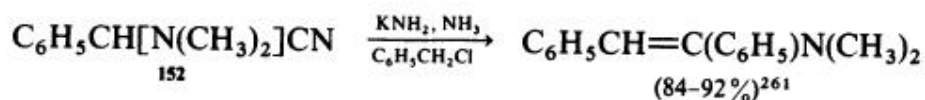
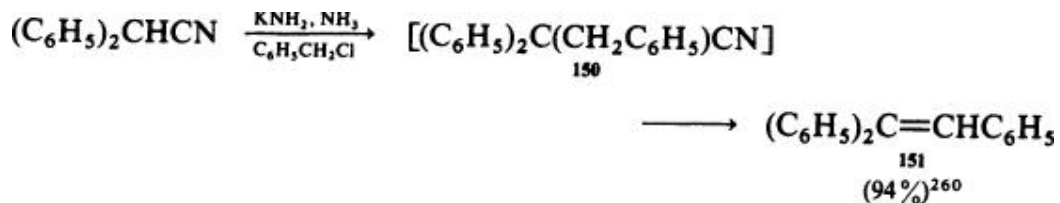
The utilization of nucleophilic bases such as sodium amide or sodium alkoxides occasionally results in the secondary conversion of a nitrile to an amidine or iminoester. In general, these troublesome additions intervene only in cases where the nitrile is disubstituted or trisubstituted and an excess of

base is present. (54, 100, 101) For example, the primary nitrile propionitrile undergoes preferential deprotonation to give the acylated product **148** in high yield, but the secondary nitrile isobutyronitrile undergoes attack at the nitrile group to give ultimately the *N*-benzoylamidine derivative **149**. (54)

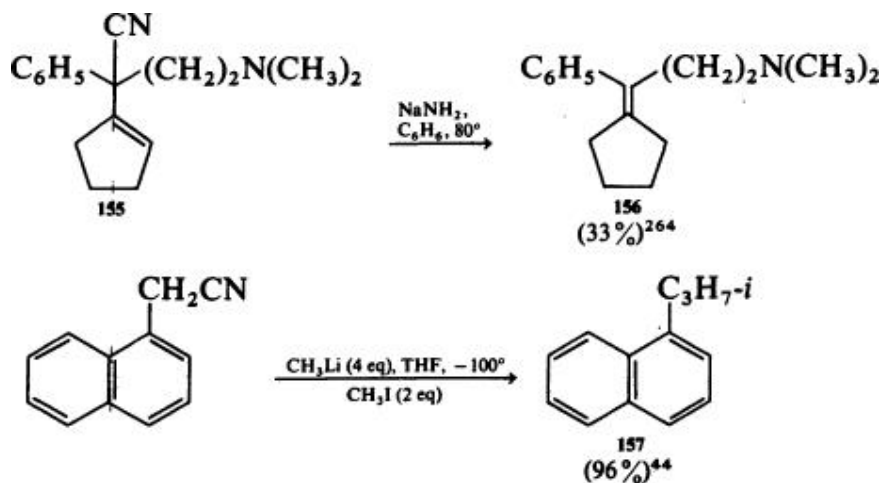


The use of nonnucleophilic bases such as lithium diisopropylamide, sodium bis(trimethylsilyl)amide, lithium triphenylmethide, or sodium hydride circumvents these problems altogether and accounts for their growing popularity for the alkylation and acylation of nitriles.

The dehydrocyanation of nitriles to alkenes occurs during nitrile alkylation in which the nitrile possesses a β -phenyl substituent and no α -hydrogens activated by the nitrile group. (110, 161, 260, 261) For example, the alkylation of diphenylacetone nitrile with benzyl chloride leads to the triphenylethylene **151** rather than the expected nitrile **150**. (260) The finding that α -aminonitriles such as **152** undergo a similar alkylation–dehydrocyanation reaction to give enamines (76, 261, 262) introduces new synthetic possibilities in that the enamine products themselves can be alkylated in a subsequent step. The dehydrocyanation of various nitriles not necessarily bearing a β -phenyl substituent provides a general enamine synthesis shown for the conversion of α -aminonitrile **153** to enamine **154**. (263) This reaction paves the way for the development of α -aminonitriles as acyl dianion equivalents. (263)

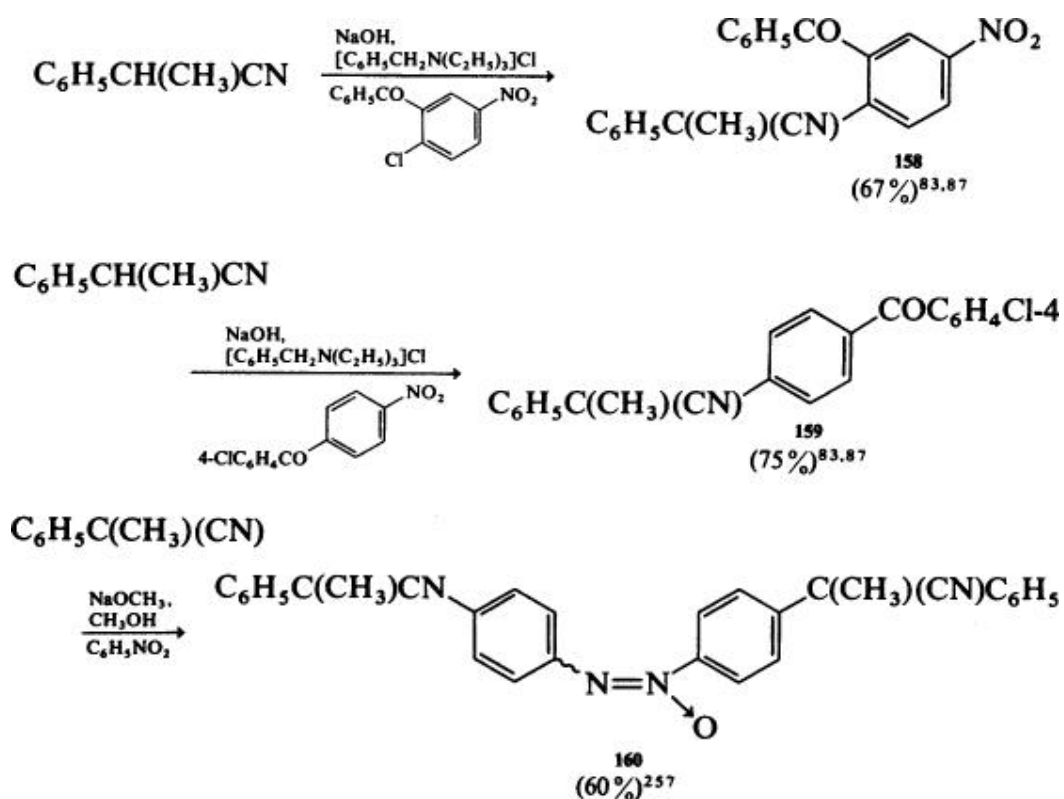


In cases where metallic sodium is used to generate the nitrile anion or where sodium amide is heated with tertiary nitriles bearing at least one α -aryl or α -heteroaryl group, (2, 264-266) the reductive decyanation of the nitrile intervenes as shown in the conversion of aminonitrile **155** to olefin **156**. (264) Although this method for generating nitrile anions has limited popularity, the reductive decyanation process has developed from a curious side reaction to a useful synthetic method. (145) Other examples of reductive decyanation include the use of methyllithium to effect both the metalation and decyanation of 1-naphthylacetonitrile to give 1-isopropylnaphthalene (**157**). (44)



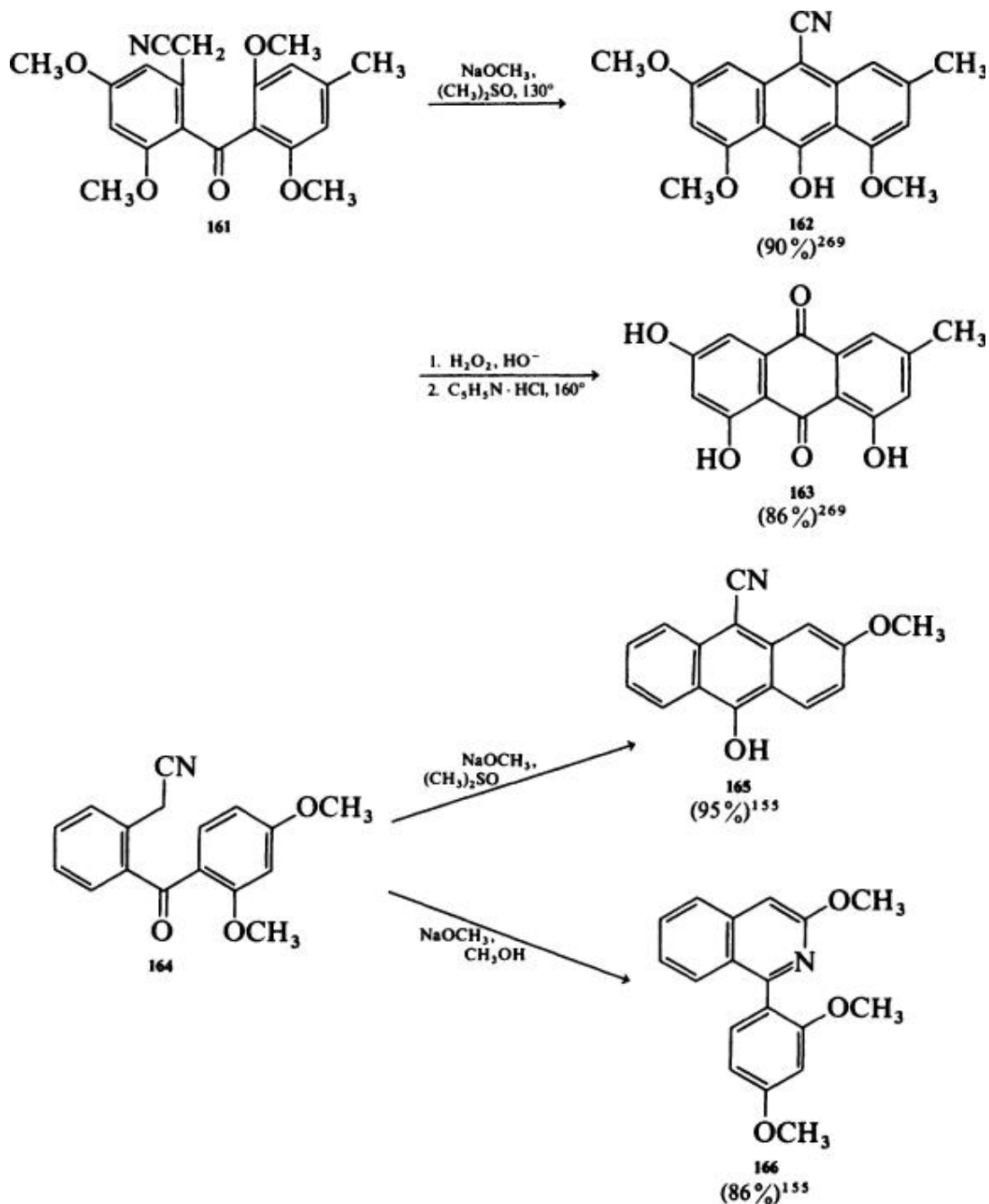
3.1.1.4. Arylation

The traditional addition–elimination mechanism for the substitution of a halogen by a nitrile-stabilized carbanion requires an aromatic ring bearing electron-withdrawing groups. The lack of a mild, direct procedure for removing typical activating groups such as the nitro group restricts the synthetic scope of the reaction, but such substitutions find application in the regiospecific synthesis of various diarylacetonitriles from phenylacetonitriles under phase-transfer catalysis conditions, as illustrated in the synthesis of **158** (83, 87) and **159**. (83, 87) Interestingly, the phase-transfer approach proves successful in certain cases where sodium amide fails to furnish the desired product. Under phase-transfer conditions, both chloro (82, 83, 86) and nitro groups (83, 87) serve successfully as leaving groups, although nitro substitution is quite limited in scope since azoxybenzene derivatives such as **160** (267) are also obtained in certain cases.

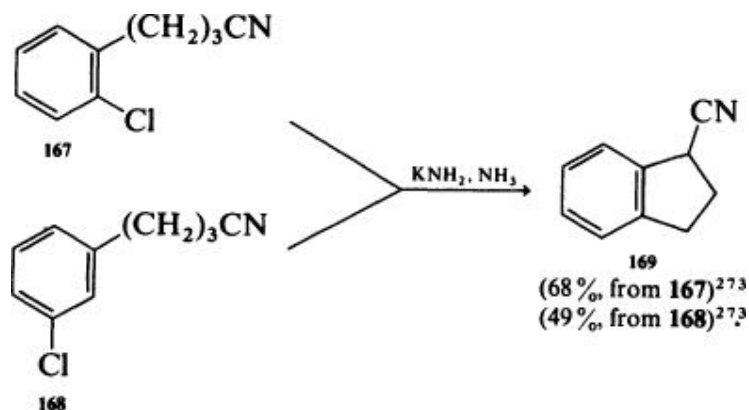


Intramolecular substitutions of a chloro or methoxy group by a nitrile-stabilized carbanion have been applied in the synthesis of highly substituted anthraquinones. (155, 268-271) In certain cases the cyclization of the nitrile anion succeeds where the analogous ester fails. Cyclization of the benzophenone **161**, for example, using sodium methoxide leads to the

cyanoanthrol **162** (**269**) in high yield. Further oxidation of the cyanoanthrols provides anthraquinones, as illustrated by the conversion of **162** to **163**. (**269**) Although a high degree of regioselectivity is noted in the cyclization of the benzophenone **161**, (**269**) other unsymmetrical examples provide mixtures. (**268**) These cyclizations generally require polar solvents such as dimethyl sulfoxide or *N,N*-dimethylformamide, and in methanol as a solvent the cyclization of the benzophenone **164** takes an entirely different course to give the isoquinoline **166** rather than the cyanoanthrol **165**. (**155**)



For substitution of halobenzenes lacking electron-withdrawing groups, the benzyne mechanism provides one avenue for attaching a nitrile-stabilized carbanion. Although the intervention of this mechanism may result in *cine*-substitution, intermolecular (141, 143, 272) examples in the literature deal only with monosubstituted halobenzenes, and, with the exception of the sodium amide-catalyzed reaction of bromobenzene with phenylacetonitrile, (143) these reactions provide only modest yields of products. In contrast, the intramolecular version of this reaction offers an efficient, flexible synthesis for the annelation of four-membered, (273-275) five-membered, (273) six-membered, (273) and seven-membered rings (273) onto an aromatic system as illustrated by the preparation of 5-cyanoindane (169). (273)

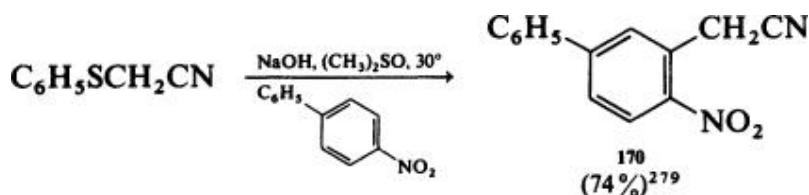


Yet another alternative for effecting the substitution of halobenzenes with nitrile anions involves the intriguing photostimulated aromatic $S_{RN}1$ reaction. (144) This radical chain reaction will accommodate the reactions of nitrile anions with halobenzenes, phenyl diethyl phosphate, and phenyltrimethylammonium iodides. (145, 276) Although the yields of substituted products are modest, this approach promises high regioselectivity in substituted cases (277) and offers considerable scope in that phenol or aniline precursors can be manipulated to furnish arylacetonitriles.

Halobenzenes activated by a π -complexed chromium tricarbonyl group (278) undergo substitution of either the halogen or a hydrogen by secondary nitrile-stabilized carbanions. (146) Attack by the anion of isobutyronitrile on the μ^6 -(chlorobenzene)tricarbonylchromium(0) (57) followed by treatment with iodine after relatively short reaction times furnishes a mixture of chloro and hydrogen substitution products 59, 60, and 61. (146) Long reaction times at ambient temperature favor the irreversible loss of chloride to give the chloro

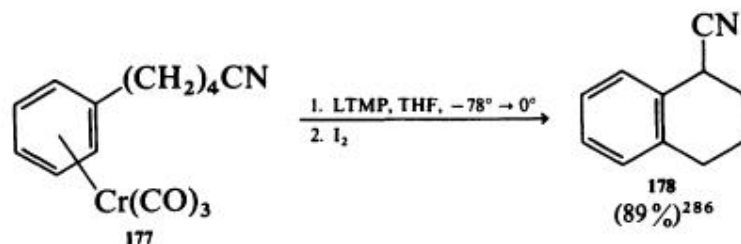
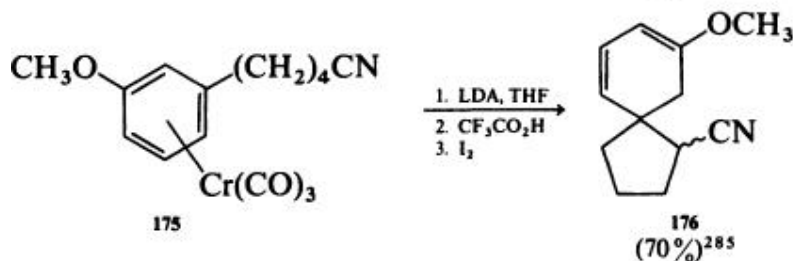
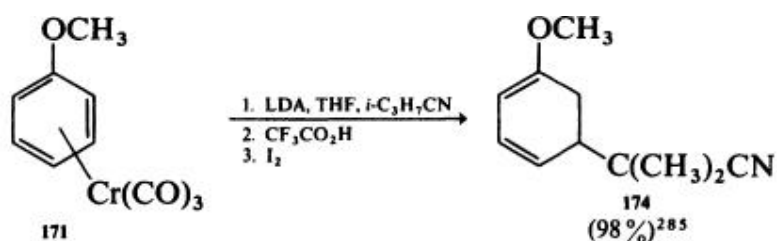
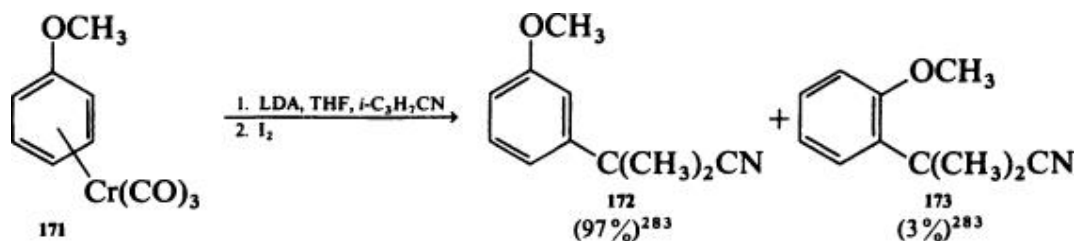
substitution product **59** as the predominant product in synthetically useful yields. The advantages offered by the use of activating metal carbonyl groups include their preparation in excellent yield under neutral conditions and their removal by use of mild oxidizing agents such as iodine.

Substitution reactions involving the formal replacement of an aromatic hydride by a nitrile anion generally involve aromatic substrates bearing electron-withdrawing groups. The addition of phenylacetonitrile anion to the *ortho* position of various *para*-substituted nitroarenes leads to benzoxazoles as illustrated by the conversion of 4-chloronitrobenzene to benzoxazole **66**. (154, 156) Similar addition of phenylacetonitrile to nitroarenes that are not substituted at the *para* position furnishes *p*-quinonemethide oximes as illustrated by the conversion of nitrobenzene to **67**. (157, 158) Similar condensations using phenylacetonitriles bearing α -alkyl substituents lead to numerous products. (267) However, acetonitriles bearing a leaving group in the α position such as an α -chloro, α -methylthio, α -phenoxy, or α -phenylthio group add to nitroarenes and subsequently expel the leaving group to give "vicarious" substitution products as illustrated by the preparation of the substituted biphenyl **170**. (279)



Several interesting hydride substitution reactions take advantage of the activating and possibly the directing influence (280) of a chromium tricarbonyl group coordinated to an aromatic ring. (146, 147, 281-285) The unsubstituted μ^6 -(benzene)tricarbonylchromium(0) intercepts a variety of primary and secondary nitrile anions, including anions of the protected cyanohydrin type. Unreactive nitrile anions are usually limited to those bearing phenyl substituents. The reaction accommodates a variety of substituents on the complexed aromatic ring that are seldom present in more traditional aromatic substitution reactions, as illustrated by the attack of isobutyronitrile anion on μ^6 -(anisole)tricarbonylchromium(0) (171) to give the *meta*-substituted and *ortho*-substituted products **172** and **173**, respectively. (146, 283) A noteworthy feature of this reaction is the high degree of *meta* regioselectivity for an aromatic ring bearing a traditional *ortho,para*-directing group. This selectivity presumably reflects the pentadienyl anion character of the transition state leading to the μ^5 -cyclohexadienyl complex. An electron-donating substituent such as the methoxy group has the least destabilizing influence in the transition

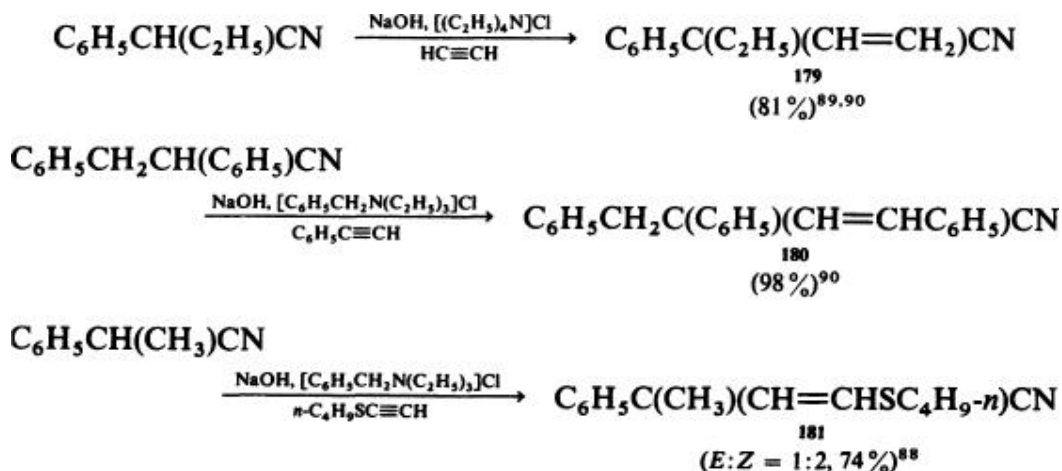
state, leading to a *meta* orientation between the substituent and the attacking nucleophile. μ^6 -Toluene- and μ^6 -*o*-dimethoxybenzenetricarbonylchromium(0) complexes also show a remarkable degree of regioselectivity. In addition to aromatic substitution, the intermediate μ^5 -cyclohexadienyl complexes provide access to products not available by traditional pathways, as illustrated by the preparation of the 1,3-cyclohexadiene **174** (**285**) from **171**. Intramolecular cyclizations of this type also provide access to either spirocyclic products such as **176** (**285**) or fused-ring products such as **178**. (**286**)



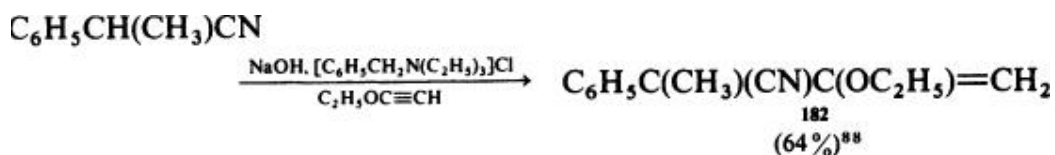
3.1.1.5. Vinylation

In contrast to the acid-catalyzed vinylation of dialkyl malonates with acetylene at high temperatures and pressure, (**287**) the base-catalyzed vinylation of nitriles provides access to interesting adducts under mild conditions. Acetylene

itself reacts with the anions of substituted phenylacetonitriles under phase-transfer conditions to furnish vinyl derivatives such as nitrile **179**. (89, 90) Substituted acetylenes, including phenylacetylene (89, 90) and *n*-butylthioacetylene, (88) add regiospecifically to nitrile-stabilized carbanions to give the 1,2-disubstituted ethylene derivatives such as **180** and **181**, respectively, as mixtures of stereoisomers in which the *Z*-isomer predominates. In contrast, ethoxyacetylene reacts, as expected, (288) with the opposite regioselectivity to give the 1,1-disubstituted ethylene derivatives as illustrated by the preparation of nitrile



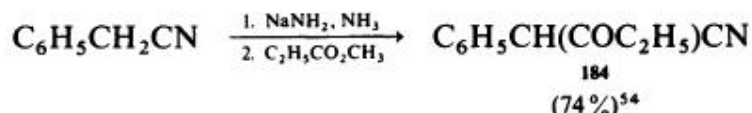
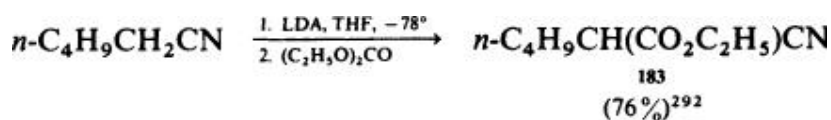
182. (88) However, the vinylation reaction of nitriles is limited in scope since 1-hexyne and diphenylacetylene fail to react. (90)



3.1.1.6. Acylation

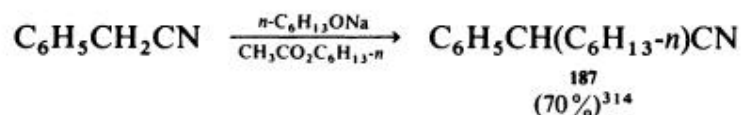
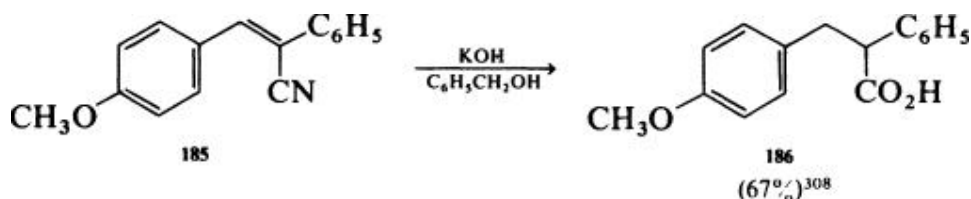
The acylation of nitrile-stabilized carbanions generally employs dialkyl carbonates, (47, 259, 289-292) chloroformates, (289, 292) carboxylic esters, (54, 258, 293-301) carboxylic anhydrides, (259, 299, 302) acid chlorides, (303, 304) or dialkyl oxalates (297, 305, 306) as electrophilic partners. Sodium amide is the base most frequently used in such acylations, and, as expected, two equivalents of base are employed in the acylation of primary nitriles since the product contains a more acidic hydrogen than the starting material. (54, 307) The acylation of secondary nitriles with the use of sodium amide is plagued by various side reactions (54) involving reaction of sodium amide with the nitrile and with the electrophilic partner. Some exceptions to this

generalization are known, as illustrated by the carboethoxylation of the secondary nitrile 2-phenylbutyronitrile with ethyl chloroformate. (289) A promising general solution to this problem employs lithium diisopropylamide and ethyl chloroformate or diethyl carbonate to effect the carboethoxylation of nitriles as in the preparation of cyanoester **183** (292) and uses sodium amide and carboxylic esters to effect the acylation of nitriles as in the preparation of β -ketonitrile **184**. (54)

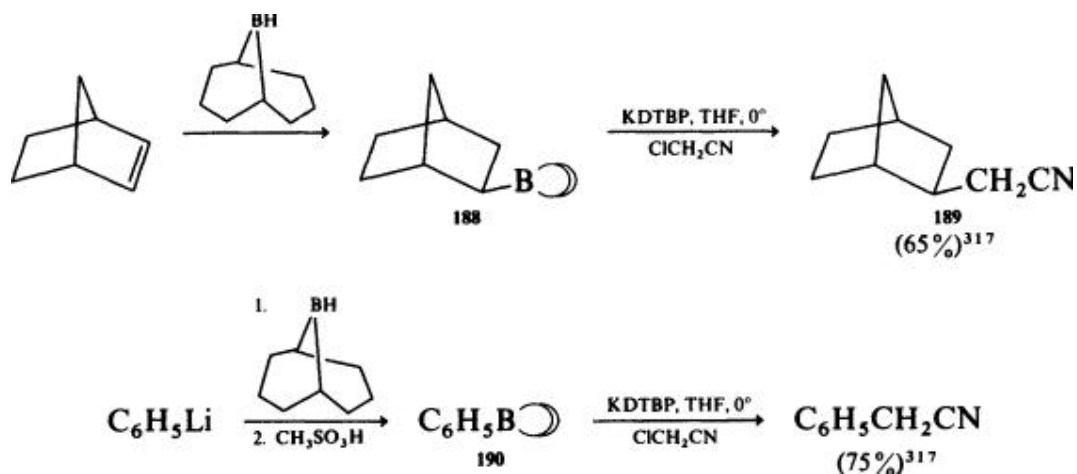


3.1.1.7. Alternative Procedures for Alkylation and Arylation of Nitriles

The condensation of nitriles with aldehydes or ketones to give acrylonitrile derivatives and the subsequent reduction of the carbon — carbon double bond provides an alternative to the direct monoalkylation of primary nitriles. This approach has the advantage of circumventing the dialkylation problem frequently encountered in the monoalkylation of primary nitriles and is illustrated by the reduction of the unsaturated nitrile **185** to the carboxylic acid **186** with the use of potassium benzylate. (308) Modifications of this approach use various sodium alkoxides to effect the reductive alkylation of phenylacetonitrile (309-314) or α -phenylacetoacetonitrile. (315) This reaction is illustrated by the conversion of phenylacetonitrile to 2-phenyloctanenitrile (**187**) (314) and relies on the Guerbet reaction to dehydrogenate the alcohol to the aldehyde and on the reduction of the acrylonitrile to generate additional aldehyde. An alternative reductive alkylation procedure for phenylacetonitrile and aldehydes uses potassium tetracarbonylhydridoferrate. (316)

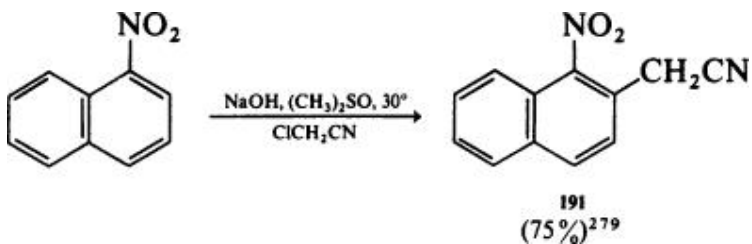


Organoboranes intercept the anions of α -chloronitriles to provide another pathway to the direct alkylation and arylation of simple nitrile anions. The addition of *B*-alkyl-9-borabicyclo[3.3.1]nonane derivatives such as **188** and **190** to the anion of chloroacetonitrile leads to alkyl- or arylacetonitriles in excellent yield. (317) This sequence, in conjunction with hydroboration, provides an overall sequence for the alkylation of acetonitrile with olefins and, as a consequence, offers certain distinct advantages with respect to stereocontrol. For example, the preparation of *trans*-(2-methylcyclohexyl)acetonitrile by use of traditional methodology requires the uncommon *cis*-2-methylcyclohexyl bromide, whereas the organoborane approach requires the readily available 1-methylcyclohexene. A similar alkylation of diazoacetonitrile with the use of organoboranes is also available. (318) Extension of this organoborane reaction to dichloroacetonitriles provides an efficient synthesis of substituted α -chloroacetonitriles, (319) which, in turn, can be alkylated to furnish various secondary nitriles.



The organoborane route for the arylation of chloroacetonitrile (317) finds an interesting parallel in the arylation of chloroacetonitrile by nitroarenes. (279) In this case, the tentative mechanism involves an *ortho* or *para* addition of α -chloronitrile anion to a nitroarene and the subsequent hydride migration to restore the aromaticity of the ring, as illustrated by the preparation of 4-nitronaphthylacetonitrile (**191**). (279) Still another cyanomethylation procedure for aromatic compounds involves the photolysis of chloroacetonitrile and aromatic substrates in acetonitrile. (320) Finally, although the focus of this chapter is base-catalyzed reactions of nitriles, the Friedel–Crafts alkylation of

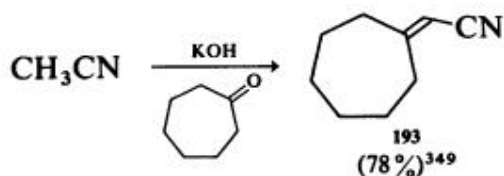
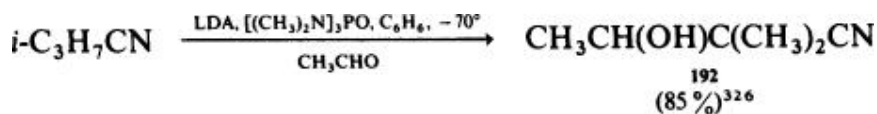
arenes with α -bromonitriles (321) also provides another route to various phenylacetonitriles.

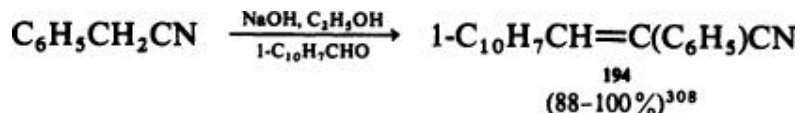


3.1.1.8. Addition to Aldehydes and Ketones

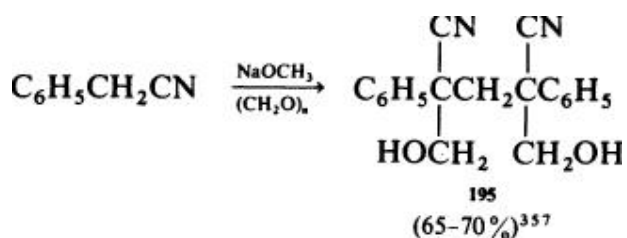
The condensation of nitrile-stabilized carbanions with aldehydes and ketones leads to either β -hydroxynitriles (19, 21, 106, 174, 322-336) or α, β -unsaturated nitriles. (250, 251, 259, 308, 337-350) Deprotonation is the usual method for generating the nitrile anions, but a Reformatsky reaction of α -chloronitriles or α -bromonitriles in the presence of zinc also provides β -hydroxynitriles (351-355) or α, β -unsaturated nitriles. (353) In general, condensations leading to β -hydroxynitriles employ relatively strong bases such as sodium amide, (106, 322, 323) lithium diethylamide, (326) sodium bis(trimethylsilyl)amide, (19) or *n*-butyllithium (106, 328, 333, 336) at low temperatures. In addition, the use of a chelating metal ion such as the magnesium salt of phenylacetonitrile furnishes acceptable yields of β -hydroxynitrile adducts, (324) although a chelating metal ion is not necessary in most instances.

Those condensations leading directly to α, β -unsaturated nitriles generally use sodium hydroxide, (308, 348) potassium hydroxide, (349, 350) sodium methoxide, (346) sodium ethoxide, (337, 339, 340, 356) or piperidine, (259) and as a consequence of using these bases, these condensations typically involve reactions of arylacetonitriles or heteroarylacetonitriles. Reactions that illustrate these generalizations include the condensations leading to the β -hydroxynitrile 192 (326) and the α, β -unsaturated nitriles 193 (349) and 194. (308)

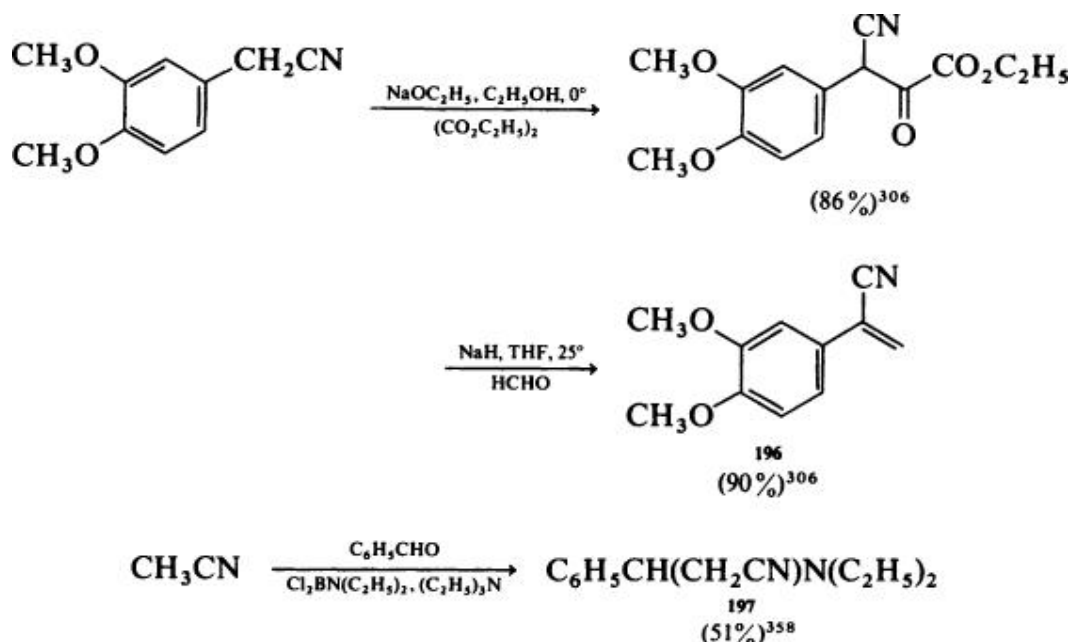




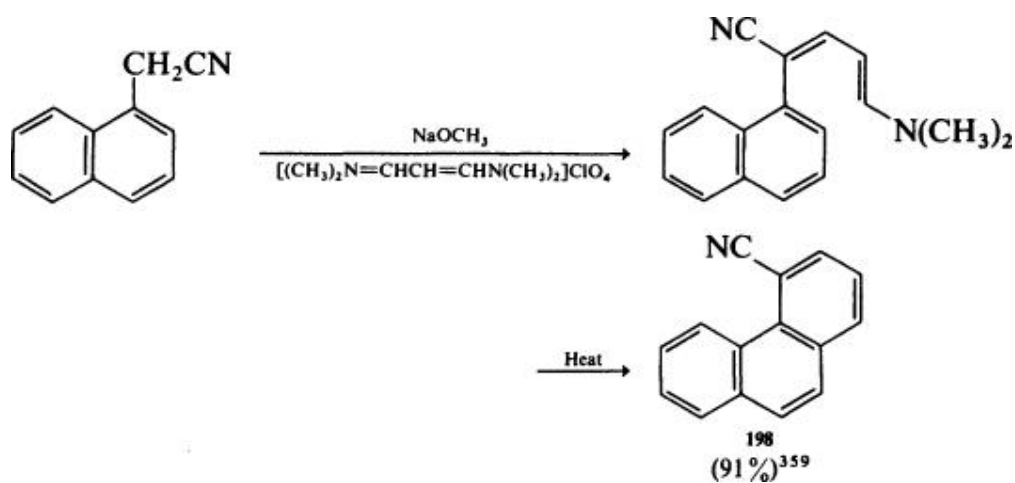
Side reactions that may complicate these condensations include self-condensation of the nitrile component, aldol condensation of the carbonyl component in the case of enolizable aldehydes and ketones, and retroreaction of the β -hydroxynitrile adduct. Occasionally, the unsaturated nitrile product undergoes further reaction, as illustrated by the abnormal condensation of phenylacetonitrile and formaldehyde to give the adduct **195**. (357)



Alternative procedures for securing unsaturated nitriles include the phosphonate Wittig condensation (12) or an acylation–alkylation sequence illustrated for the preparation of α -(3,4-dimethoxyphenyl)acrylonitrile **196**. (306) A variant of the condensation of nitriles with carbonyl compounds involves the reaction of a diethylaminodichloroborane–nitrile complex with aldehydes in the presence of triethylamine to give modest yields of the β -(dialkylamino)nitriles as illustrated for the preparation of **197**. (358) Another procedure for synthesizing



related β -(dialkylamino)nitriles involves the condensation of nitriles with immonium salts that constitutes a useful annelation procedure, as illustrated in the case of 4-phenanthrenecarbonitrile (**198**). (359)



3.1.1.9. Addition to Nitriles

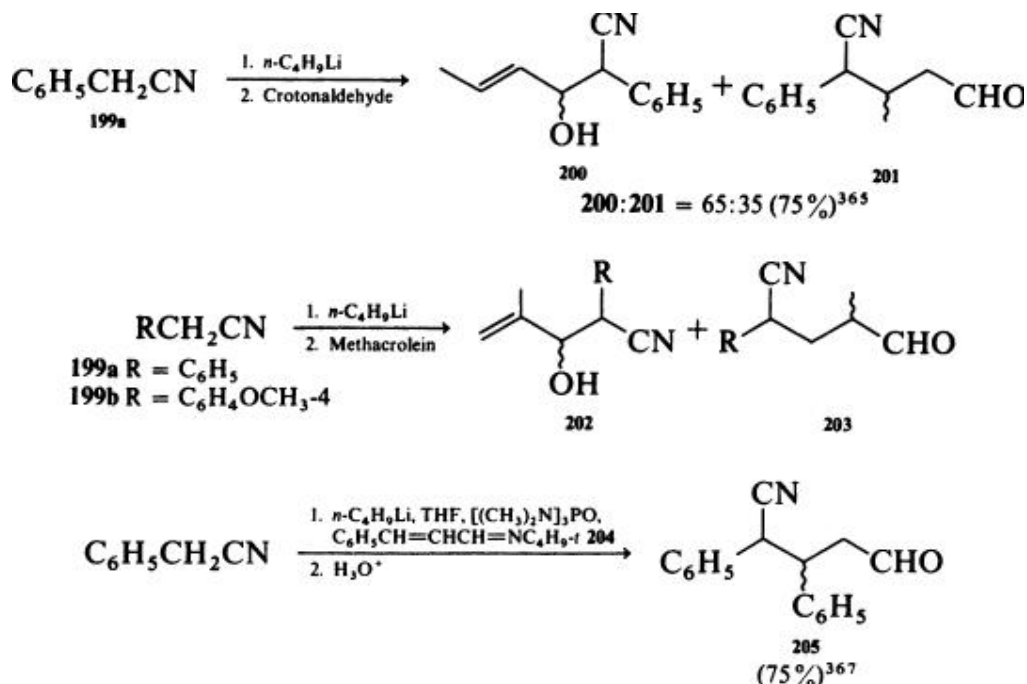
The well-known Thorpe–Ziegler condensation is applied in the synthesis of medium-ring and large-ring compounds and has been the subject of a review (257) in this series. The limited interest (21, 258, 360-363) in the intermolecular condensations of nitriles stems from the obvious problems presented by cross-coupling reactions between different nitriles and from

alternative routes for preparing β -ketonitriles that do not involve a nitrile electrophile.

3.1.1.10. Addition to Various Michael Acceptors (364)

The regioselectivity of the addition of nitrile anions to α, β -unsaturated aldehydes and ketones varies as a function of substrate and nitrile structure, reaction temperature, and solvent. For α, β -unsaturated aldehydes, the kinetically controlled 1,2-addition products predominate in reactions conducted and quenched at low temperature in ether solvents. (365, 366) For example, the addition of the anion of phenylacetonitrile to crotonaldehyde in tetrahydrofuran at -70° gives predominantly the diastereomeric allylic alcohols **200** in 75% yield. (365) An exception to this generalization is the addition of the anion of phenylacetonitrile to methacrolein, where the 1,4 adduct **203** predominates even at low temperatures. (365)

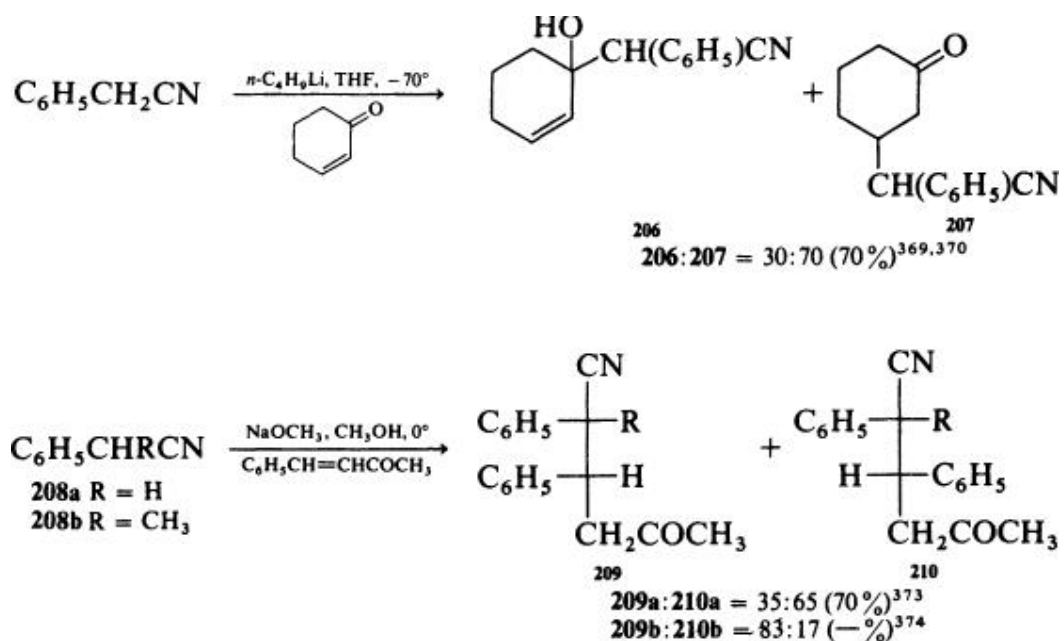
To shift the product distribution in favor of the thermodynamically controlled 1,4-addition product, either the temperature of the reaction is elevated or a polar cosolvent such as hexamethylphosphoramide is added to the reaction medium. (365, 366) For example, the dramatic influence of temperature on the product distribution is illustrated by the exclusive isolation of the diastereomeric 1,4 adducts **201** in the addition of phenylacetonitrile to crotonaldehyde in the -30° -to- 0° range. (365, 367) A preference for 1,4 addition is also observed in reactions of nitrile anions with α, β -unsaturated imines, provided the β carbon of the imine is, at most, monosubstituted. (367) For example, the addition of phenylacetonitrile to the unsaturated imine **204** provides the 1,4 adduct **205**. (367)



The 1,4-addition products of nitrile anions and unsaturated aldehydes represent either thermodynamic and/or kinetic products depending on the structure of the nitrile. In the case of the 1,2 adduct **202a** of phenylacetone nitrile and methacrolein, the addition of hexamethylphosphoramide to a solution of the lithium alkoxide of **202a** at -70° renders the 1,2-addition reaction reversible and furnishes a 65 : 35 ratio of the 1,2 adduct and 1,4 adduct **202a** and **203a**, respectively. (365) In the case of 4-methoxyphenylacetone nitrile (**199b**), the addition of hexamethylphosphoramide to a solution of the lithium alkoxide of the 1,2 adduct **202b** does not alter the product distribution, implying that the 1,2-addition reaction is irreversible for this nitrile even in the presence of hexamethylphosphoramide. However, if the addition of the anion **199b** to methacrolein is conducted in a medium where hexamethylphosphoramide is present from the outset, a 60:40 ratio of the 1,2- and 1,4-addition products **202b** and **203b** is obtained. (365) Similar and, in certain cases, more dramatic illustrations that the 1,4-addition product also represents a kinetic product have been observed (366) and the inability of the lithium cation to complex with the phosphoryl group in hexamethylphosphoramide provides an explanation for kinetic 1,4 addition in this medium. (368) From a synthetic perspective, the ability to alter regiochemistry in favor of 1,4 addition by varying temperature and solvent represents a useful synthetic device.

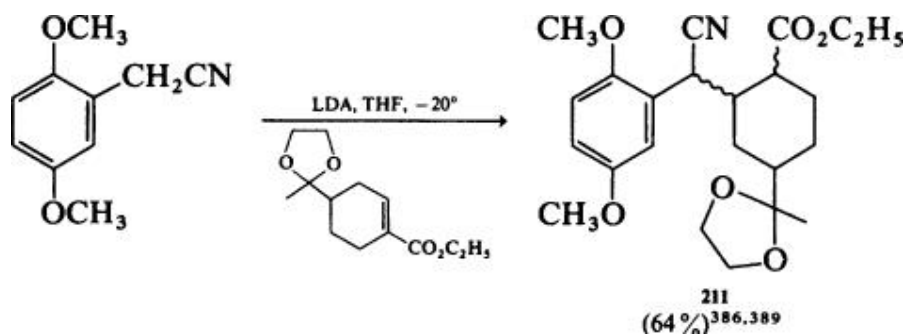
In the case of α, β -unsaturated ketones, the regioselectivity of the addition of nitrile anions is complicated by the relative instability of the 1,2 adducts

compared to the 1,2 adducts derived from α , β -unsaturated aldehydes. For example, under conditions where unsaturated aldehydes give exclusively 1,2 adducts, the addition of the anion of phenylacetonitrile to 2-cyclohexenone gives a 30:70 ratio of the 1,2 and 1,4 adducts **206** and **207**, respectively. (369, 370) Shorter reaction times give a higher proportion of the kinetic 1,2-addition product than in the above reaction but still do not provide the predominant 1,2 regioselectivity noted in aldehyde cases. (365) Predominant 1,2 regioselectivity is noted, however, in addition of the anion of phenylacetonitrile to mesityl oxide in the presence of zinc chloride. (376) The increased reversibility of the tertiary alkoxides derived from ketones relative to the secondary alkoxides derived from aldehydes is consistent with other literature reports (371, 372) and substantiated by the addition of hexamethylphosphoramide as a cosolvent in which case the 1,4 adducts are obtained exclusively. (369, 370) The stereoselectivity in the Michael addition of either phenylacetonitrile (373) or 2-phenylpropionitrile (374) to *trans*-4-phenyl-3-buten-2-one varies considerably, as shown by the equilibrium mixtures of diastereomeric products **209** and **210**. In contrast to the reactions of arylacetonitriles, the anion of acetonitrile undergoes exclusive 1,2 addition to 2-cyclohexenone. (369) Similar 1,2 additions of aliphatic nitriles to benzylideneacetophenone have also been reported. (375) The effect of elevated reaction temperatures or polar cosolvents on the product distribution from aliphatic nitriles is as yet unknown.



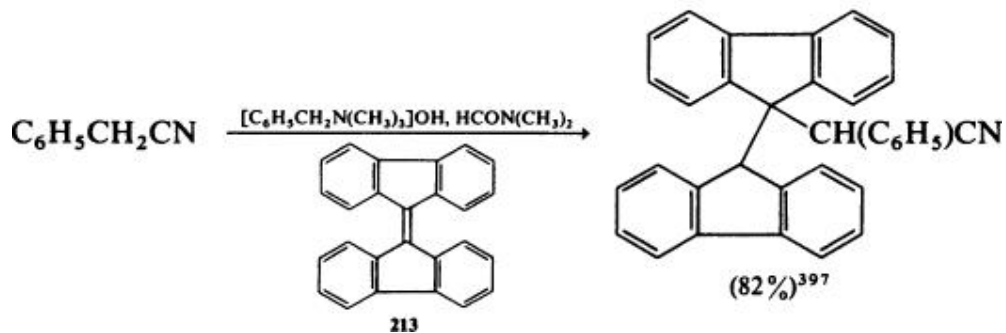
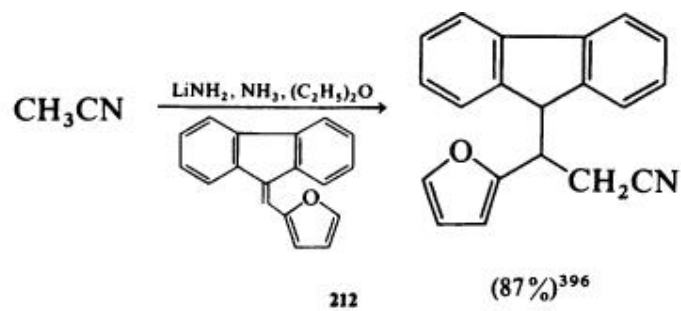
The reactions of nitrile-stabilized carbanions with unsaturated esters, (52, 229, 377-390) unsaturated nitriles, (341, 377) unsaturated sulfones, (391) and

unsaturated nitro compounds (392-395) proceed largely in a 1,4 sense and only in certain cases involve competitive 1,2 and 1,4 addition. (295) Unlike nitrile anion additions to α , β -unsaturated aldehydes and ketones, low temperatures favor 1,4 addition over 1,2 addition, and in cases where the addition of the nitrile anion to the unsaturated ester is sluggish at -78° , warming to -20° to 0° is usually sufficient to effect 1,4 addition, as illustrated by the preparation of γ -cyanoester **211**. (386, 389) The 1,4 additions of nitrile-stabilized anions to α , β -unsaturated esters and nitro compounds find application in the synthesis of anthracyclines (388, 390) and aromatic D-homosteroids. (393, 394)

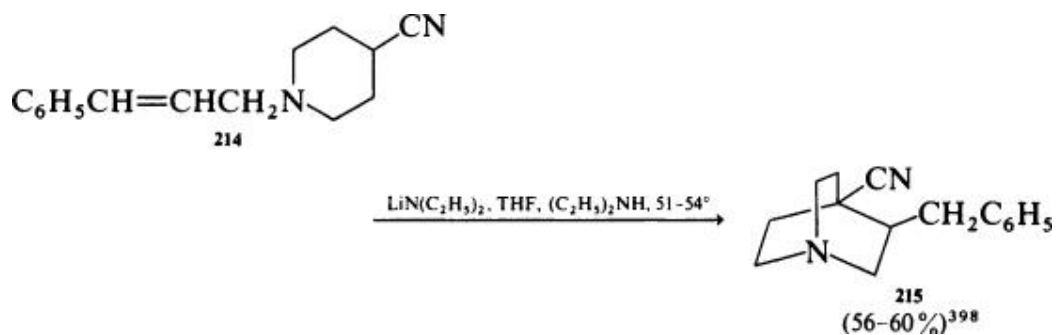


3.1.1.11. Addition to Olefins

The traditional Michael addition (364) of nitrile anions to enones occurs with selected olefins. Since the pK_a of 9-alkylfluorenes is less than the pK_a of aliphatic nitriles, the addition of the corresponding nitrile anions to 9-benzylidene fluorene, (396) 9-furfurylidene fluorene (**212**), (396) and—in certain cases—benzylideneindene, (396) gives the expected adducts. A similar addition of the anion of phenylacetonitrile to 9,9-bifluorenylidene (**213**) gives

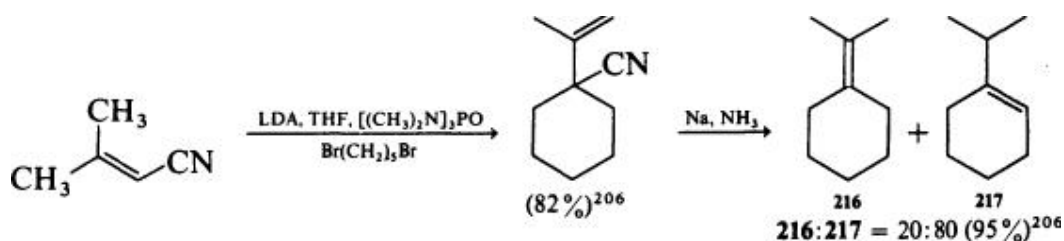


the expected adduct. (397) An interesting intramolecular addition to the styrene moiety in **214** produces the quinuclidine **215**. (398)

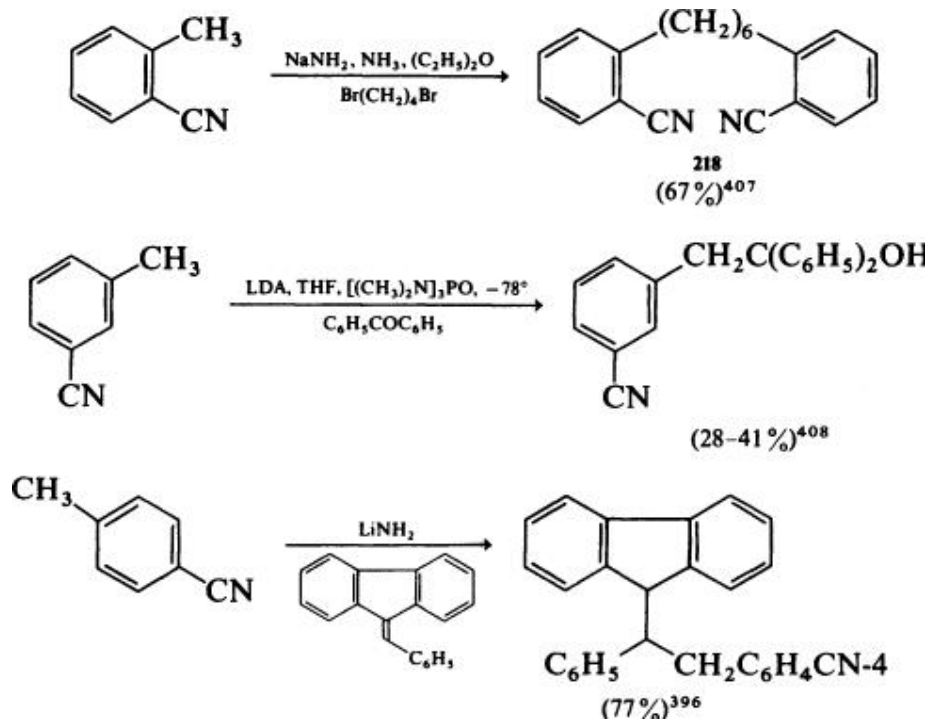


3.2. Reactions of Unsaturated Nitrile-Stabilized Carbanions

The monoanions and dianions derived from aliphatic α, β -unsaturated or β, γ -unsaturated nitriles exhibit a marked α regioselectivity for either monoalkylation (198, 339, 399-401) or dialkylation (44, 103, 165, 206, 402-404) with various alkyl halides. The monoanions of unsaturated nitriles are generated by use of sodium or potassium hydroxide, (400-404) sodium naphthalide, (198) sodium amide, (399, 402, 403) or lithium diisopropylamide; (165, 206, 399, 401) the dianions are generated by using *n*-butyllithium. (44, 103) In general, the best yields are obtained with the use of lithium diisopropylamide in an aprotic medium containing hexamethylphosphoramide. The polar cosolvent ensures a high concentration of the nitrile anion and precludes self-condensations leading to polymeric material. (401) The dialkylation of unsaturated nitriles in conjunction with the reductive decyanation of the tertiary nitrile products represents a useful procedure for the synthesis of isopropylidene-substituted cycloalkanes as illustrated by the preparation of **216**. (206)



The metalation of tolunitriles generates another type of unsaturated nitrile-stabilized carbanion that for obvious reasons does not exhibit the usual α regioselectivity. The anions derived from *ortho*-tolunitrile, *meta*-tolunitrile, and *para*-tolunitrile undergo alkylation with alkyl halides, (405-408) activated olefins, (396) or ketones; (406, 408) arylation with aryl halides; (409) and acylation with carboxylic esters. (405, 406) The stabilizing influence of the cyano group is clearly greatest for the *ortho* and *para* isomers, which are conveniently metalated by alkali metal amide and dialkylamide bases. The *meta* isomer is metalated by use of lithium diisopropylamide. The best yields of alkylated products are obtained by simultaneously adding 3-tolunitrile and the electrophile to a solution of the base. (408) Unlike the arylacetonitriles, the alkylation of the tolunitriles gives no dialkylated products, presumably because of the reduced acidity and/or nucleophilicity of the monoalkylated products. For example, the dialkylation of 2-tolunitrile with 1,4-dibromobutane furnishes only the bis derivative **218** (407) and not 2-(cyanophenyl)cyclopentane.



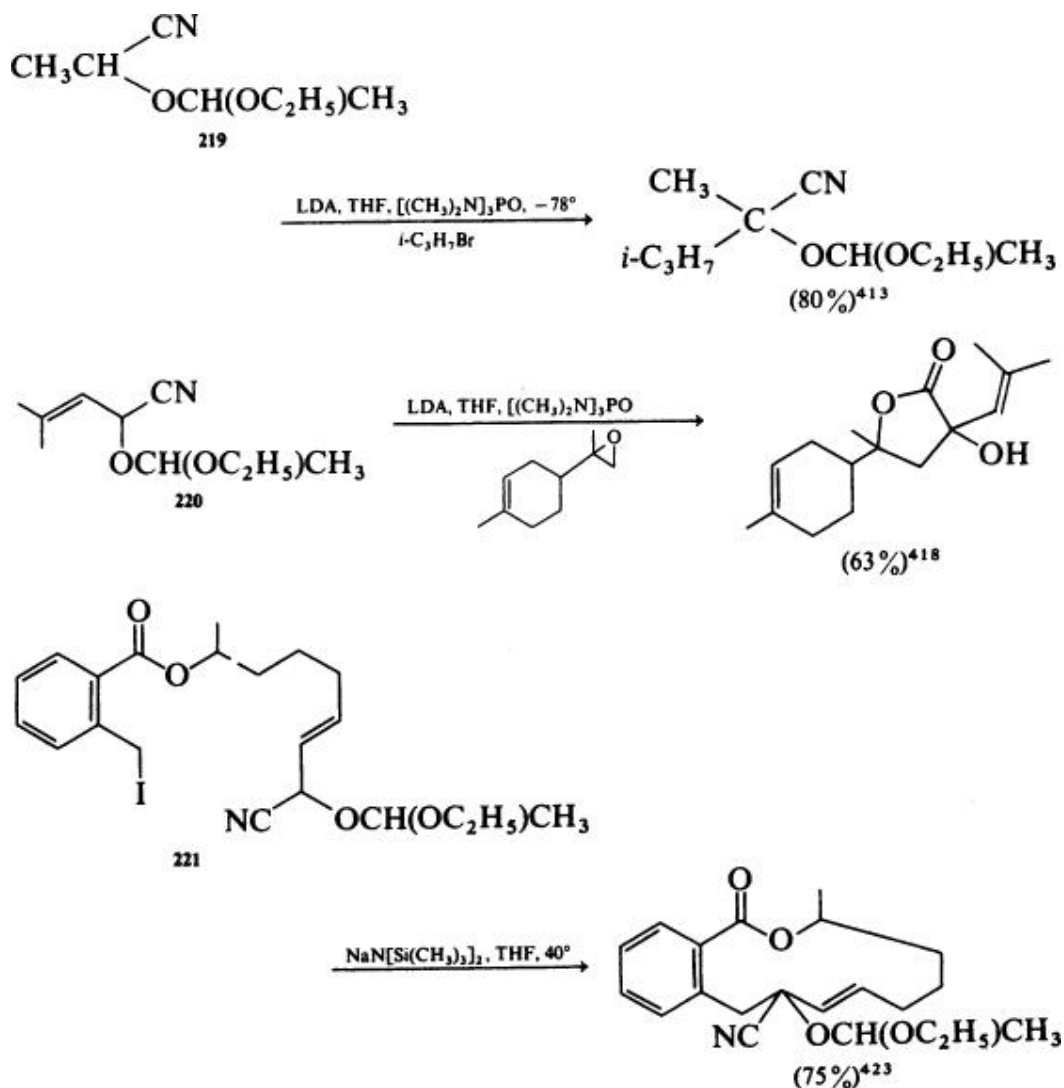
3.3. Reactions of Protected Cyanohydrin Anions

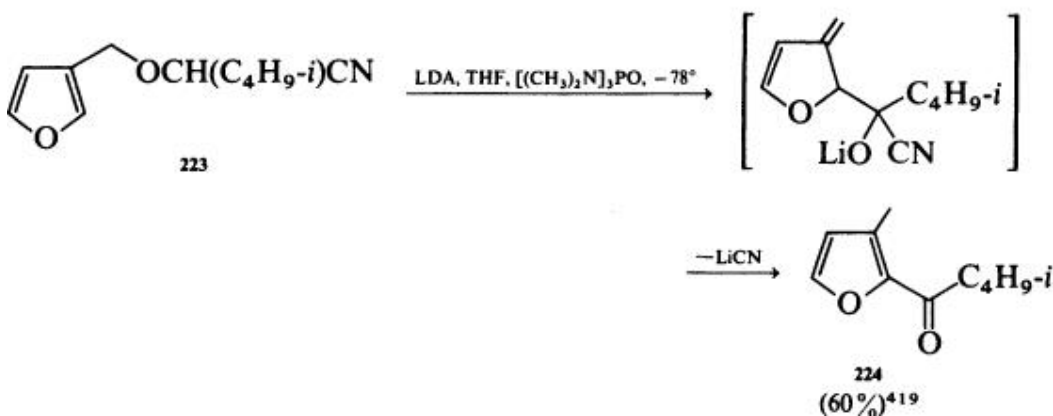
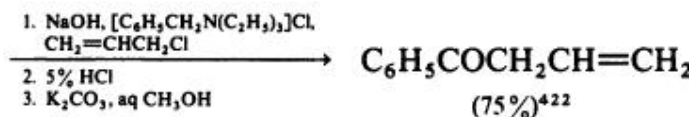
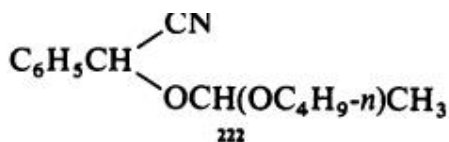
3.3.1.1. Alkylation

Acyl carbanion equivalents (410-412) represent a broad class of synthetic intermediates in which the nucleophilic center possesses a latent carbonyl group. The well-known interconversion of cyanohydrins and carbonyl compounds suggests that the carbanions of protected cyanohydrins would provide a masked nucleophilic carbonyl derivative. This inversion from that normally associated with the carbonyl group has greatly expanded the utility of carbonyl compounds in organic synthesis.

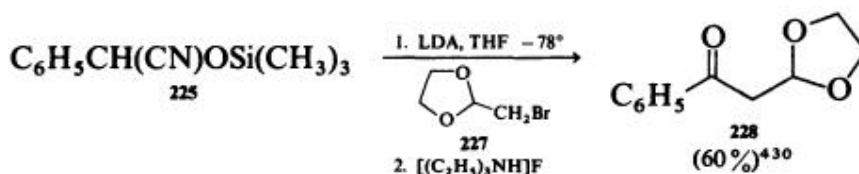
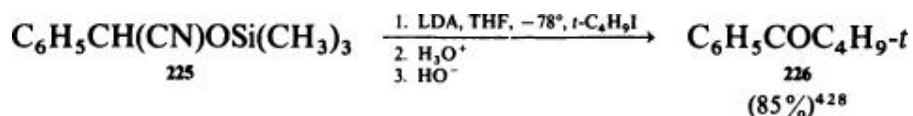
The addition of aliphatic, aromatic, or heteroaromatic cyanohydrins to ethyl vinyl ether, (413-421) *n*-butyl vinyl ether, (422) or dihydro-4*H*-pyran (414) provides a base-stable, protected cyanohydrin derivative. The successful metalation of these protected cyanohydrins, alkylation with alkyl halides, (413-417, 419-421) alkyl sulfonates, (416) or epoxides (418) and, finally, hydrolysis of the product furnishes an array of ketones in good overall yields. Typically, lithium diisopropylamide is used to generate the nitrile anion, but sodium methylsulfinylmethide (414) is also used. Sodium hydroxide under phase-transfer conditions is an alternative for protected cyanohydrins derived from aromatic or heteroaromatic aldehydes. (422) These methods are illustrated by the alkylation of the saturated, aliphatic cyanohydrin derivative 219 with an alkyl halide, (413) the alkylation of the unsaturated, aliphatic

cyanohydrin derivative **220** with an epoxide, (**418**) the intramolecular alkylation of **221**, (**423**) and the alkylation of the aromatic, protected cyanohydrin **222**. (**422**) Additional alkylations involving the methyl, (**194**) ethyl, (**424**) phenyl, (**194**) or benzyl (**194**) ethers of cyanohydrins are known but appear to offer no advantages over the acetal-protected cyanohydrins. One interesting reaction sequence, however, employs a furylmethyl ether in the protected cyanohydrin **223** in conjunction with a [2,3]-sigmatropic rearrangement to achieve a synthesis of elsholtzia ketone (**224**). (**419**) Finally, although the protected cyanohydrin route displays considerable scope for the synthesis of ketones, the extension of this approach to the protected derivatives of glycolonitrile fails and thus eliminates the use of these reagents for the synthesis of aldehydes.

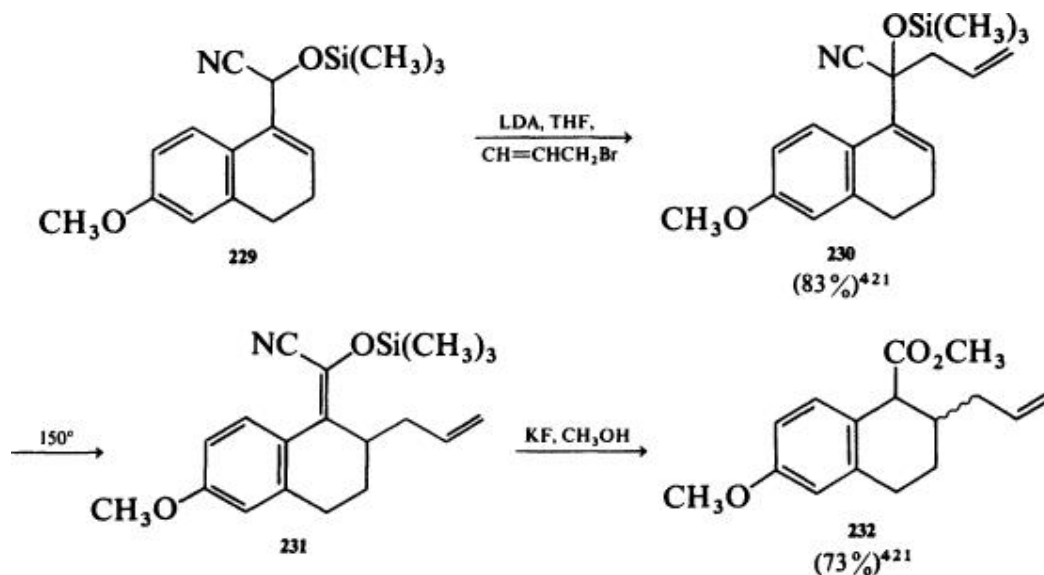




An alternative to the use of acetal-protecting groups for cyanohydrins involves the *O*-trimethylsilyl ethers, which are readily prepared from aldehydes by use of cyanotrimethylsilane. (425-427) The alkylation of *O*-trimethylsilyl ethers of either unsaturated aliphatic aldehydes (416, 421) or aromatic aldehydes (428-430) with alkyl halides, alkyl sulfonates, and dialkyl sulfates displays considerable scope, but unlike the acetal-protected cyanohydrins, the alkylation of *O*-trimethylsilyl ethers of saturated aldehydes fails. For example, the anion of 2-(trimethylsilyloxy)-2-phenylacetonitrile (225) reacts with primary, secondary, and remarkably with tertiary alkyl halides (139, 428) to give ketones, as illustrated by the preparation of *tert*-butyl phenyl ketone (226). (428) The use of trialkylammonium fluorides to deblock the protected cyanohydrin is sufficiently mild to preserve other reactive functionality in the molecule, as illustrated by the alkylation of the anion of 225 with 2-(bromomethyl)-1,3-dioxolane (227) to give the ketoacetal 228. (430)



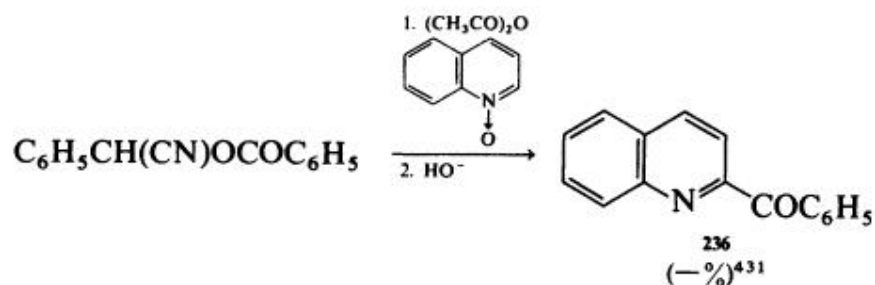
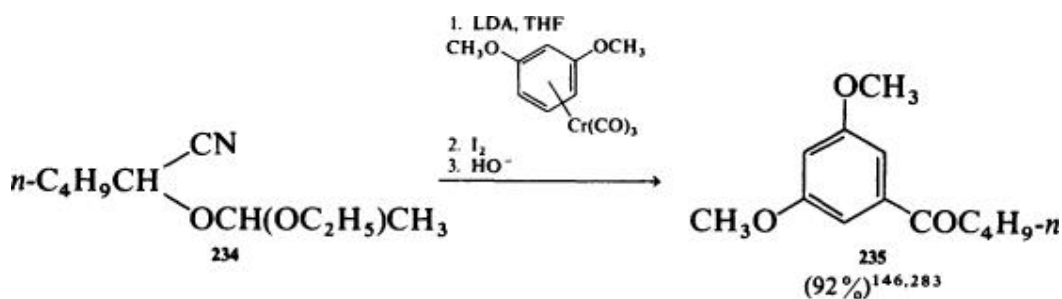
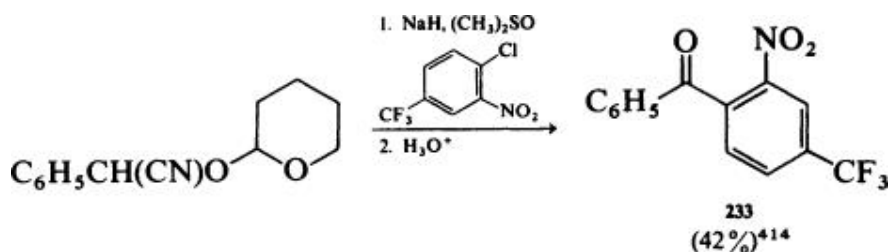
The conversion of α , β -unsaturated aldehydes to their protected cyanohydrins and the metalation of these derivatives generates anions that are capable of reacting with electrophiles at either the α or γ position. In reactions with alkyl halides, a high degree of α regioselectivity is noted for either acetalprotected (413, 415, 417, 418) or trimethylsilyl ether-protected (416, 421, 428) cyanohydrins of this type. The hydrolysis of these α -alkylated products provides access to a variety of unsaturated ketones, and, in an interesting case, the α -alkylation of the protected cyanohydrin 229 in conjunction with the Cope rearrangement produces the product 231, which, in turn, furnishes the δ , ϵ -unsaturated ester 232. (421)



3.3.1.2. Arylation

The classic $S_N\text{Ar}$ substitution of activated aryl halides by protected cyanohydrin anions provides substituted benzophenones (194, 414) in modest

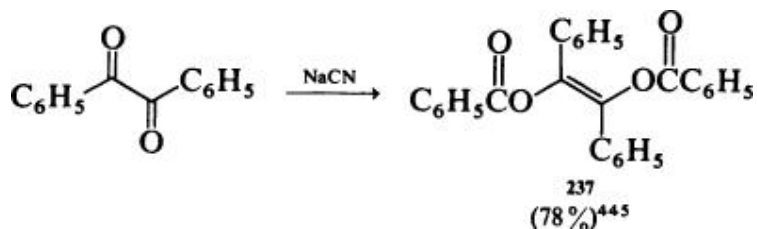
yield, as illustrated by the preparation of **233**. (414) Another procedure for the arylation of protected cyanohydrin anions involves the use of aromatic substrates activated as their π -chromium tricarbonyl complexes. (146, 283) Addition of the anion of **234** to the 1,3-dimethoxybenzene complex leads, for example, principally to the *meta*-substituted isomer **235**. Preferential *meta* regioselectivity is also noted with other π -chromium tricarbonyl complexes of arenes. Other arylation reactions of cyanohydrin anions include interesting but synthetically limited additions to quinoline *N*-oxides to give substituted quinolines such as **236**. (431)



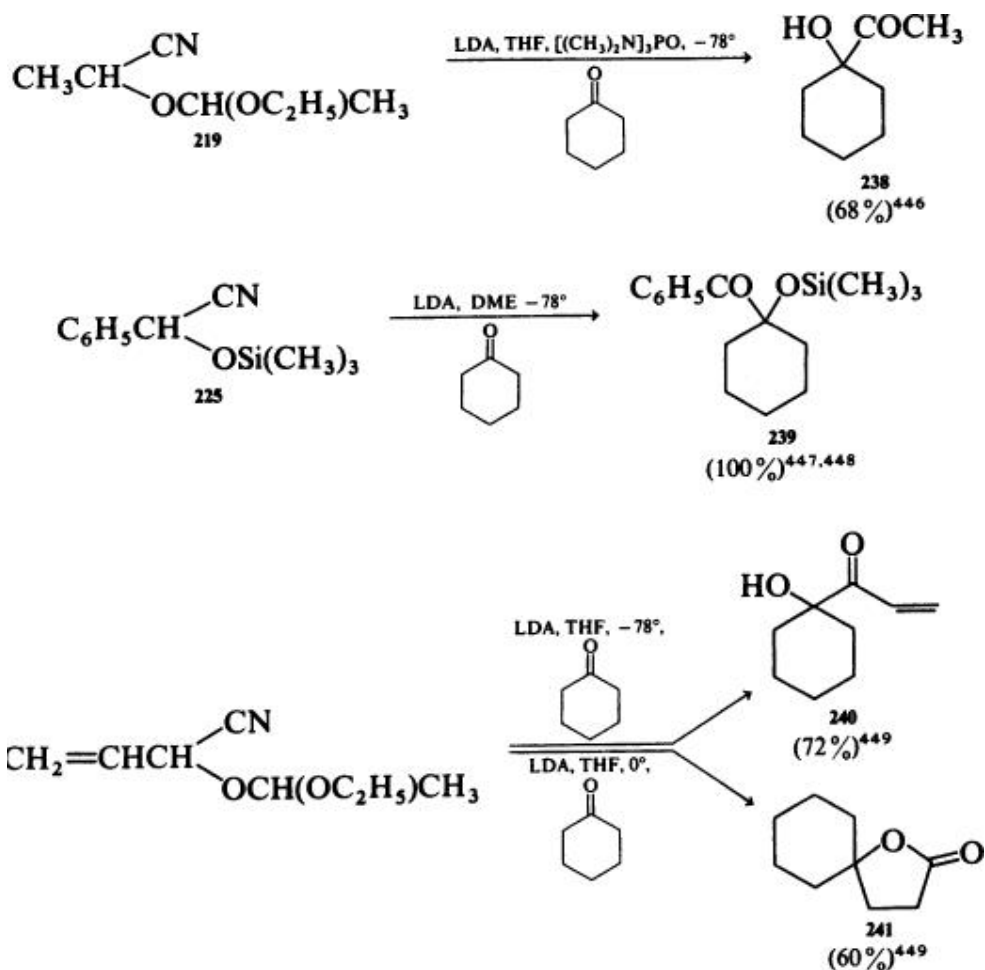
3.3.1.3. Addition to Aldehydes and Ketones

The benzoin condensation (432, 433) represents the forerunner of the acyl anion equivalents of the protected cyanohydrin type and in various forms, continues to find application in synthesis. (434-442) The condensations of anions of cyanohydrins themselves with other aldehydes and Michael acceptors is necessarily restricted to the cyanohydrins of nonenolizable

aromatic or heteroaromatic aldehydes where the weak base sodium cyanide generates the necessary anion. Other base-labile cyanohydrin derivatives such as the *O*-benzoates of mandelonitrile also employ the mild base potassium carbonate in condensations with aliphatic aldehydes. (443) Alternatively, the reaction of cyanide with benzil is used to generate a similar intermediate anion that condenses with aliphatic and aromatic aldehydes (444) to give the expected products or, in a curious reaction, with benzil itself (445) to give the stilbenediol dibenzoate **237**.



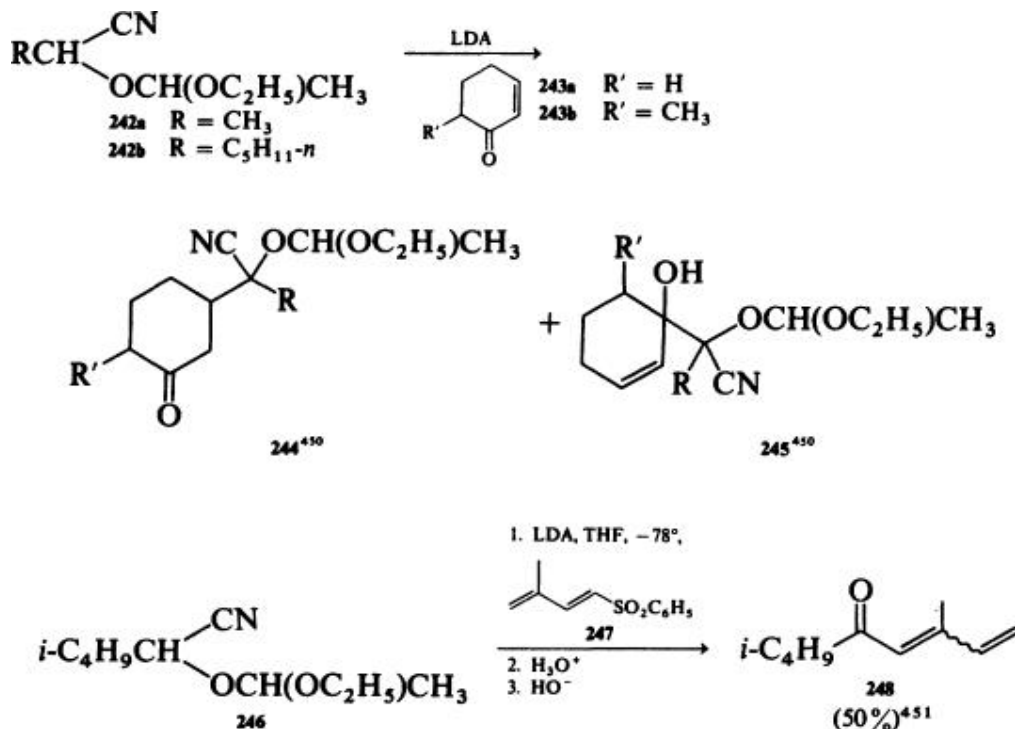
The condensation of acetal-protected cyanohydrins derived from saturated aliphatic aldehydes with aldehydes or ketones provides α -hydroxyketones. (446) The reaction of the protected cyanohydrin **219** with cyclohexanone, for example, provides 1-acetylcyclohexanol (**238**). (446) The corresponding derivatives of aromatic aldehydes do not, however, undergo successful additions. (446) In the case of the *O*-trimethylsilyl ether-protected cyanohydrins derived from aromatic aldehydes, condensation with aldehydes and ketones, followed by an intramolecular migration of the trimethylsilyl group and elimination of cyanide, does give the expected α -trimethylsilyloxy ketones. (447, 448) For example, the condensation of the cyanohydrin derivative **225** with cyclohexanone gives the α -trimethylsilyloxy ketone **239**. (447) Finally, the condensation of the *O*-trimethylsilyl ether-protected cyanohydrins derived from unsaturated aldehydes with aldehydes and ketones displays a kinetically controlled α regioselectivity at -78° , as illustrated by the preparation of α -hydroxyketone **240**. (449) In contrast, the addition to these same electrophiles at 0° shows thermodynamically controlled γ regioselectivity, as illustrated by the preparation of γ -lactone **241**. (449)



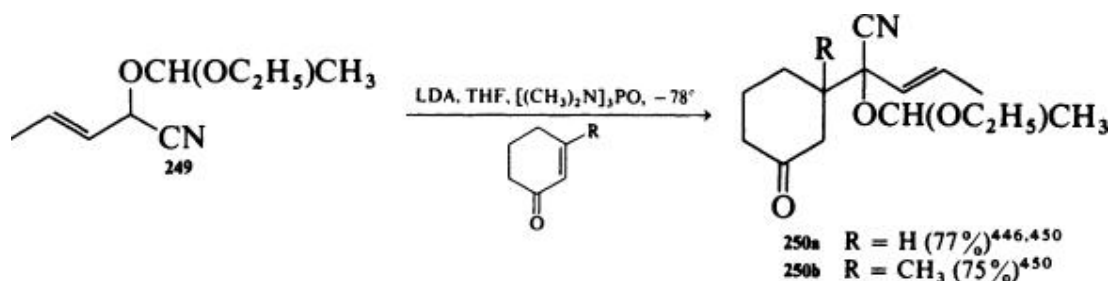
3.3.1.4. Addition to Various Michael Acceptors

The anions of protected cyanohydrins derived from saturated aliphatic aldehydes undergo competitive 1,2 and 1,4 addition to unsaturated electrophiles. The proportion of the two adducts appears to vary as a function of both structure and solvent. Steric interactions that favor dissociation of the reversibly formed 1,2-addition product increase the proportion of the 1,4-addition product. For example, increasing the size of the substituent R in a protected cyanohydrin **242** from a methyl group in **242a** to an *n*-pentyl group in **242b** increases the ratio of 1,4-addition product **244** to 1,2-addition product **245** from 1.5 to 2.7 in reactions with cyclohexenone (**243a**). (450) This ratio also increases from 1.5 to 6 in going from cyclohexenone (**243a**) to 6-methylcyclohexenone (**243b**) by use of the nitrile anion **242a**. (450) Finally, the addition of the anion **242a** to 3-methylcyclohexenone gives, as expected, almost exclusively the 1,2-addition product. (446, 450) An interesting variant of these Michael-type additions involves the 1,6 addition of the anion of **246** to the unsaturated sulfone **247** as a route to the dienone **248**. (451) Finally, the

cyanide-catalyzed addition of unprotected cyanohydrins to enones or acrylonitriles proceeds in a 1,4 sense to give 1,4-diketones but is necessarily restricted to cyanohydrins of aromatic (435, 436, 452) or heteroaromatic (434-436) systems.

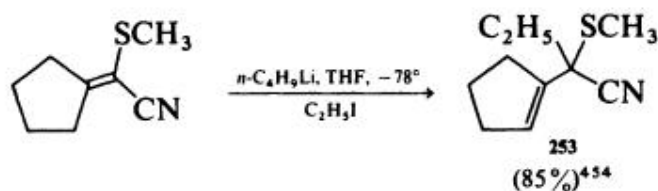
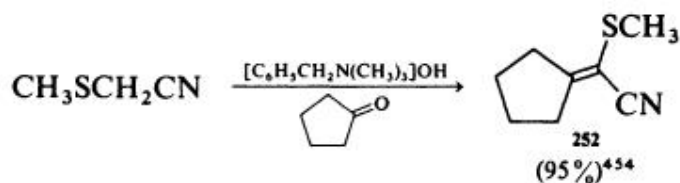
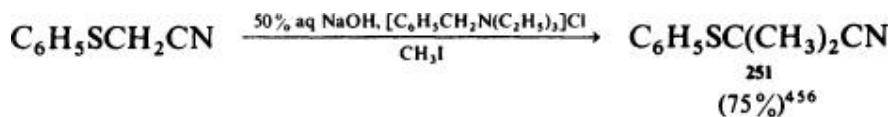


The anions of protected cyanohydrins derived from unsaturated aldehydes react with unsaturated electrophiles with α regioselectivity with respect to the anion and with 1,4 regioselectivity with respect to the electrophile. For example, the protected cyanohydrin **249** derived from crotonaldehyde adds to cyclohexenone and 3-methylcyclohexenone to give the 1,4 adducts **250a** and **250b**, respectively. (450) This result is in marked contrast to the addition of anions of saturated aldehydes to these same enones where considerable 1,2 addition is noted. The reported conditions (450) under which the anions of unsaturated, protected cyanohydrins add to enones are similar to conditions where these same anions exhibit γ regioselectivity in addition to ketones. (449, 453) A consistent mechanistic picture for both substrates may involve the reversible 1,2 addition of the anion of **249** at 0° with γ regioselectivity followed by a Cope rearrangement to the observed 1,4-addition product **250** in the case of unsaturated enones.

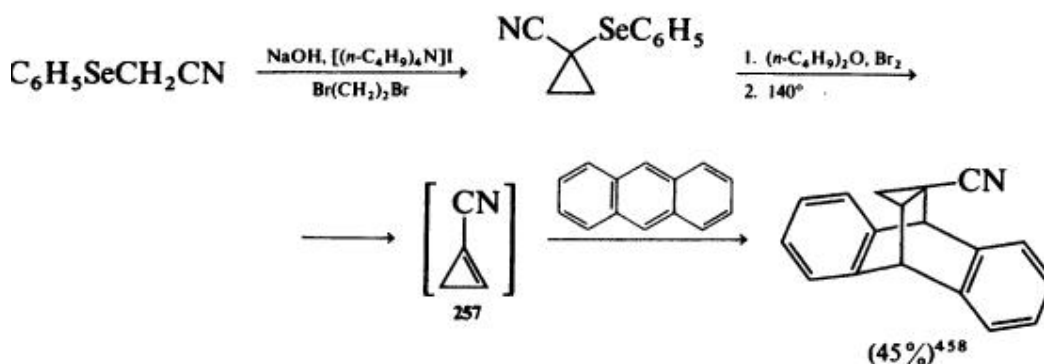
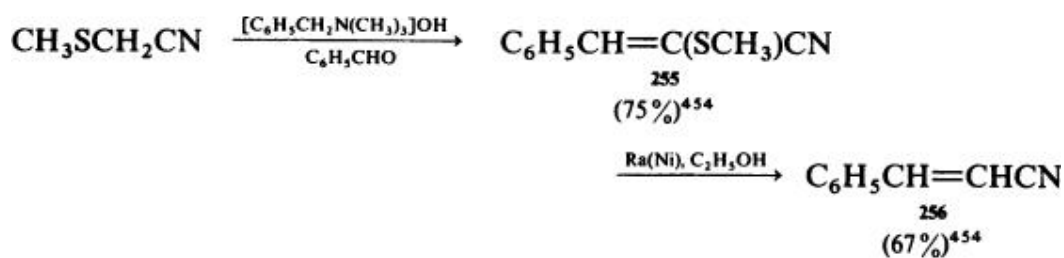
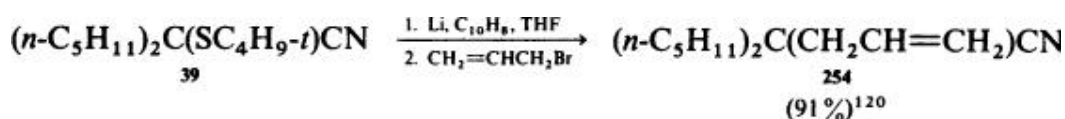


3.4. Reactions of Protected Thiacyanohydrins or Selenacyanohydrin Anions

The alkylation of nitriles bearing α -sulfur or α -selenium substituents offers the advantage that the heteroatom provides more stabilization for these carbanions than the corresponding cyanohydrins. As a consequence, mild bases such as potassium hydroxide, (454) sodium hydroxide under phase-transfer conditions, (455-459) and benzyltrimethylammonium hydroxide (454) effect deprotonation of cyanomethyl dimethyldithiocarbamate, (457) S-cyanomethyl diethylthiocarbamate, (457) cyanomethyl methyl sulfide, (454) cyanomethyl phenyl sulfide, (456, 459) and cyanomethyl phenyl selenide. (458) Examples illustrating such alkylations with alkyl halides and carbonyl compounds include the preparation of 251 (456) and 252. (454) Alternatively, lithium amide (120) and lithium diisopropylamide (460) also deprotonate α -sulfur-substituted or α -selenium-substituted nitriles. Regioselective α alkylations of α -alkylthioacrylonitriles employ *n*-butyllithium for deprotonation, as illustrated in the preparation of 253. (454)



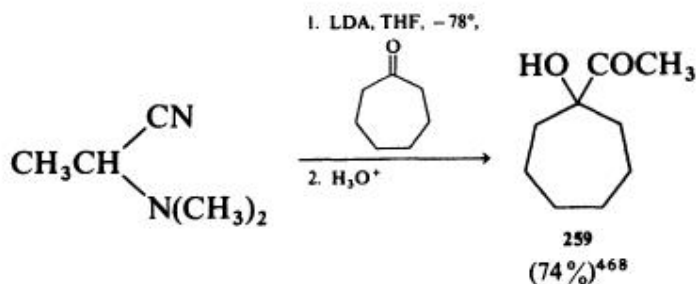
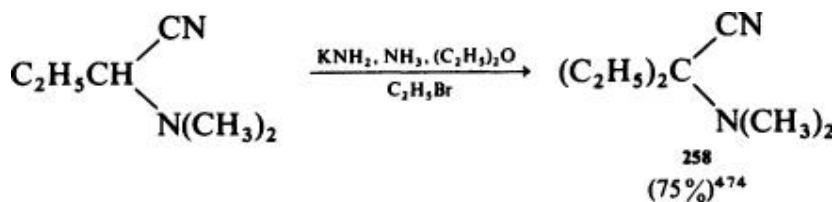
In addition to the high yields of alkylation products, the most attractive feature of these reagents stems from the synthetic versatility of the sulfur-containing or selenium-containing substituent. Desulfurization of either α -(alkylthio)acetonitriles (120) or α -(alkylthio)acrylonitriles (454) provides access to various mono- and dialkylated acetonitriles and acrylonitriles, respectively. For example, the reductive alkylation of α -(*tert*-butylthio)acetonitrile 39 with lithium in tetrahydrofuran containing catalytic amounts of naphthalene or trimesitylborane provides the trialkylated acetonitrile 254. (120) No comparable process is available in the α -oxygen-substituted or α -nitrogen-substituted nitrile families. Simple reductive desulfurization of α -methylthioacrylonitriles such as 255 using Raney nickel (454) furnishes acrylonitriles and offers an alternative to the phosphonate Wittig reaction (12, 13) for the preparation of acrylonitriles. Finally, oxidative elimination of the methylthio (454) or phenylselenenyl groups (458) provides access to various acrylonitriles, as illustrated by the generation of 1-cyclopropenecarbonitrile (257). (458)



3.5. Reactions of α -(Dialkylamino)nitrile-Stabilized Carbanions

From a historical perspective, the α -(dialkylamino)nitrile anions were the first acyl anion equivalents to undergo systematic investigation. (261, 461-463)

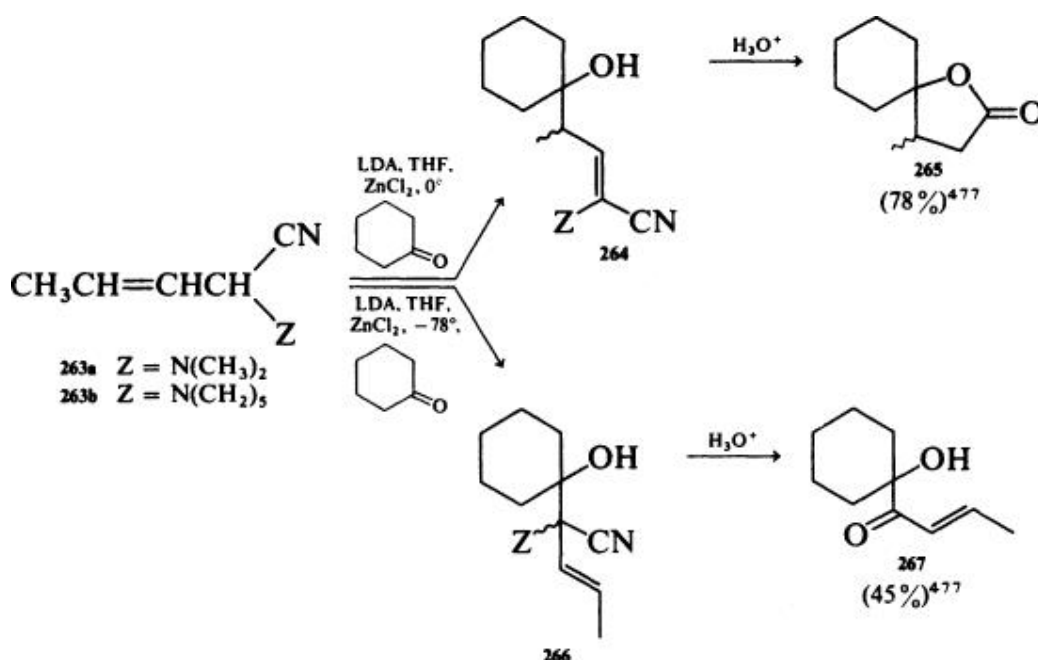
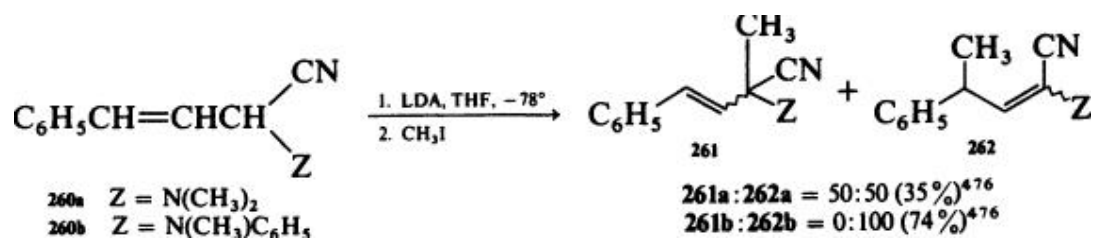
More recent studies indicate that anions of α -(dialkylamino)nitriles derived from saturated aliphatic, aromatic, or heteroaromatic aldehydes intercept an array of electrophiles, including alkyl halides, (76, 262, 263, 464-466) aryl halides, (466) alkyl sulfonates, (465) epoxides, (465) aldehydes, (467, 468) ketones, (468) acid chlorides, (466) chloroformates, (466) unsaturated ketones, (465, 469) unsaturated esters, (470) and unsaturated nitriles. (470-473) For example, the alkylation of such anions with alkyl halides and ketones is illustrated by the preparation of **258** (474) and **259**, (468) respectively.



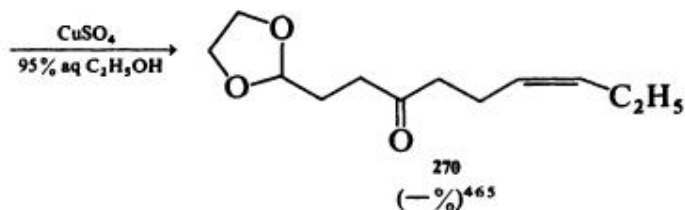
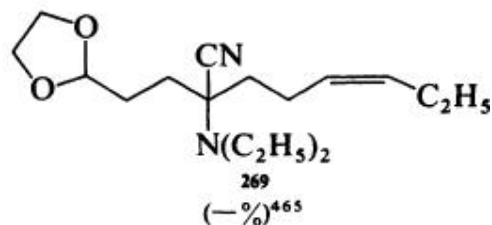
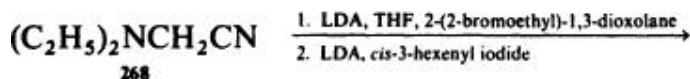
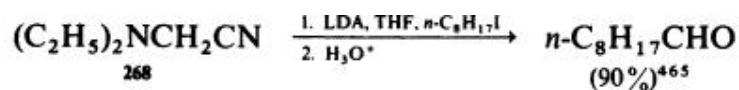
Anions of substituted α -(dialkylamino)acrylonitriles or their β , γ -unsaturated counterparts also react with alkyl halides, (475, 476) ketones, (476, 477) and unsaturated ketones (475) with predominant γ regioselectivity. This result contrasts with the α regioselectivity observed with the α -oxygen-substituted or α -sulfur-substituted acrylonitriles. The substituents on the nitrogen in α -(dialkylamino)-acrylonitriles have a pronounced influence on the ratio of α -alkylation and γ -alkylation products. (476) For example, the α -(dimethylamino) derivative **260a** furnishes the α -alkylated and γ -alkylated products **261a** and **262a**, respectively, in a 50:50 ratio, whereas the *N*-methylaniline derivative **260b** gives exclusively the γ -alkylated product **262b**. (476) The addition of aldehydes (476) or ketones (476, 477) to the anions of α -(dimethylamino)acrylonitrile **263a** or the analogous piperidine derivative **263b** at 0° leads to γ -alkylated products such as **264**, (477) which is conveniently isolated as the γ -lactone **265**. (477) The same additions at -78° furnish the kinetically controlled α -alkylated adducts **266**, as illustrated by the preparation of the α' -hydroxyenone **267**. (477)

Advantages associated with the use of α -(dialkylamino)nitrile anions include

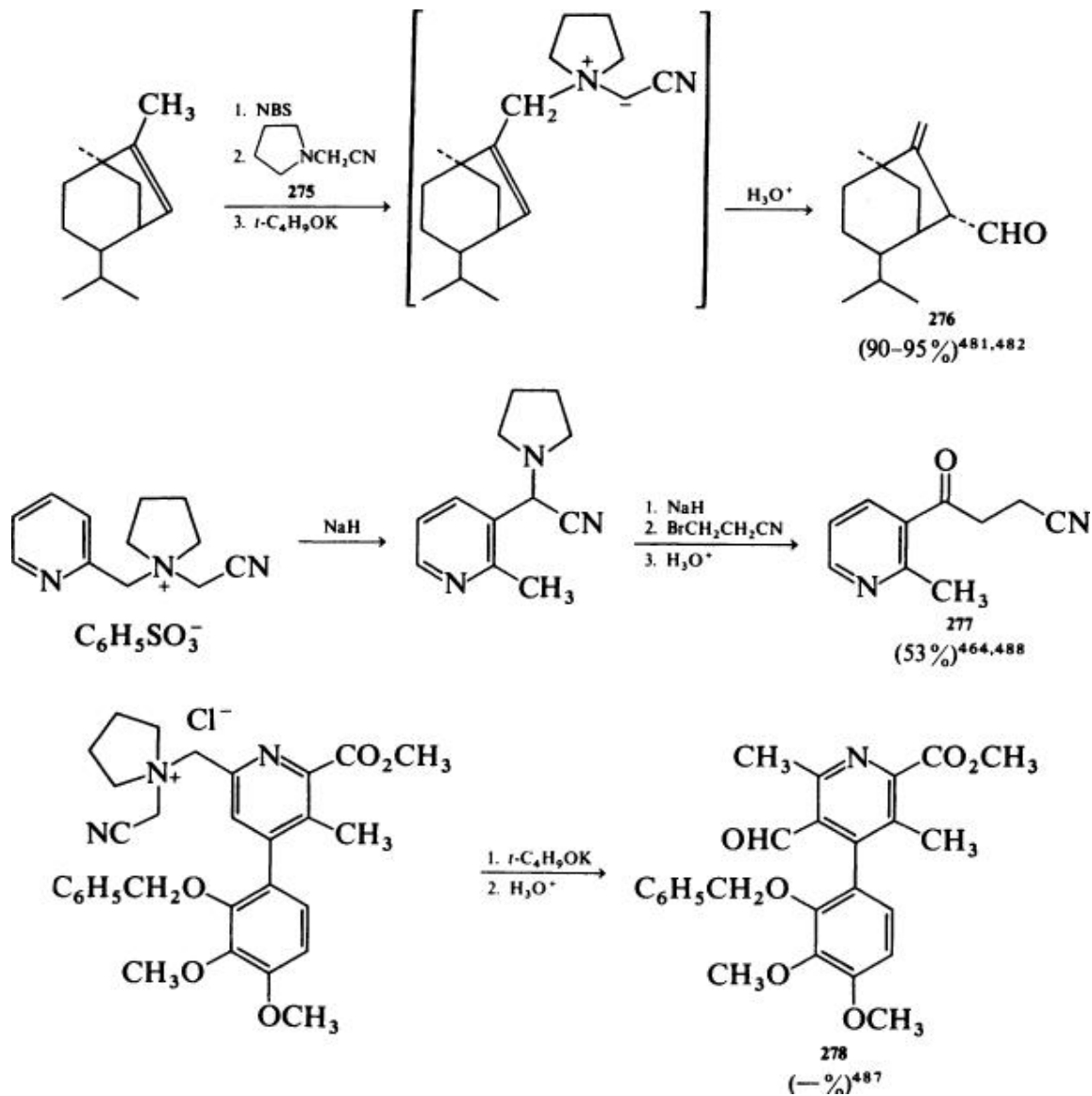
the synthesis of both aldehydes and ketones in contrast to the acyl anions in the cyanohydrin family, which cannot be used to prepare aldehydes. For example, the one-carbon homologation of *n*-octyl iodide by use of *N,N*-diethylaminoacetonitrile



(268) gives nonanal in excellent yield. (465) With the use of this same reagent, the sequential dialkylation of 268 furnishes the ketone 270. (465) The use of copper sulfate as a cyanide sequestering agent (465, 478) in the hydrolysis of α -(dialkylamino)nitriles is a mild hydrolysis method that in the case of 269 (465) avoids concomitant acetal hydrolysis.

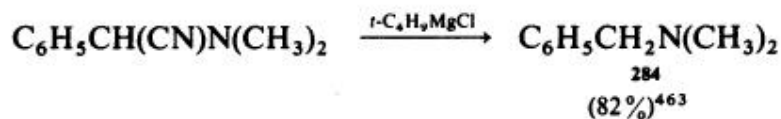
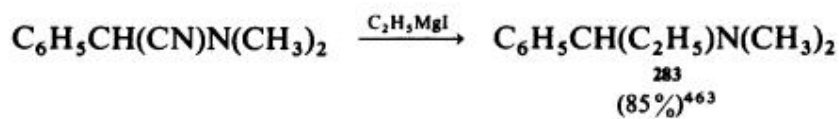
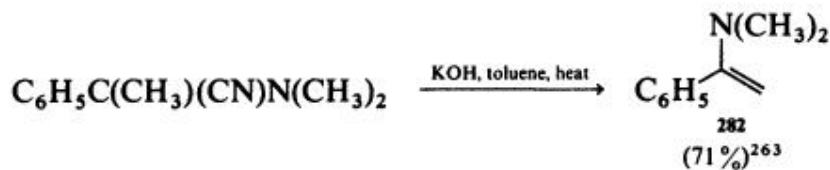
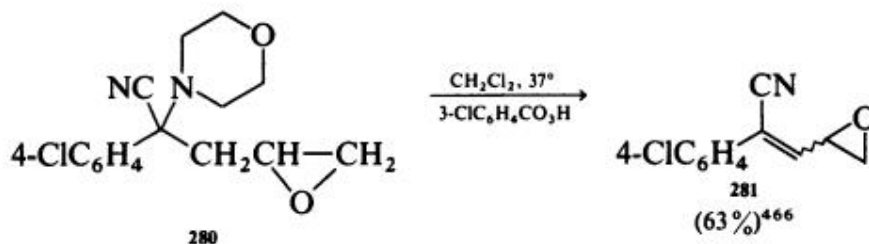
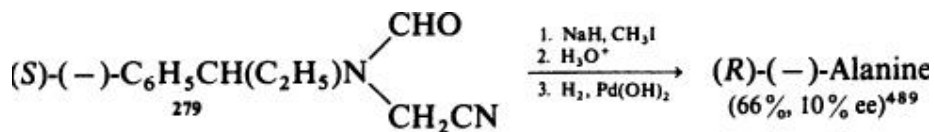


It is also significant that the anions of α -(dialkylamino)nitriles undergo 1,4 addition to various Michael acceptors (465, 469-473) in marked contrast to the 1,3-dithiane anions, which undergo preferential 1,2 addition. For example, the condensation of 271 with methyl vinyl ketone furnishes the 1,4 adduct 272. (465) However, condensations with enones having two β -alkyl groups give, as expected, predominantly 1,2 addition. (475) Further examples that highlight the utility of α -(dialkylamino)nitriles include the addition of *N,N*-diethylamino-acetonitrile (268) to epoxides to provide an overall sequence for the carbonylation of olefins (465) and the addition of *N*-(methyleneamino)acetonitrile (273) to aldehydes to furnish a one-carbon homologation procedure for the synthesis of acids. (479) Finally, the addition of the anion of α -(dialkylamino)acrylonitriles to Michael acceptors proceeds with γ regioselectivity for the nucleophile and 1,4 regioselectivity for the electrophile, as illustrated in the preparation of the ketone 274. (475)



Several additional interesting reactions conspire to make α -(di-1-pyrrolidino)-nitriles particularly valuable in comparison with other acyl anion equivalents. For example, the use of chiral α -aminonitriles such as the *N*-formyl derivative **279** allows an asymmetric synthesis of alanine albeit in low optical yield. (489) Oxidation of the amino substituent in the α -aminonitrile **280** and thermal elimination of the *N*-oxide provides a route to unsaturated nitriles such as **281**. (466) Finally, the cyano group in α -(di-1-pyrrolidino)nitriles undergoes elimination on treatment with potassium hydroxide in refluxing toluene to give enamines, (261, 263) undergoes substitution by an alkyl group on treatment with a Grignard reagent derived from a primary alkyl halide, (461, 463, 490-492) or exhibits reductive decyanation on treatment with

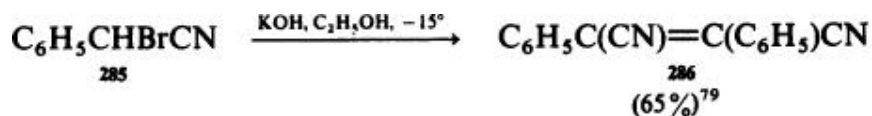
tert-butylmagnesium chloride. (463) The preparations of **282**, (263) **283**, (463) and **284** (463) illustrate these various reactions.



3.6. Reactions of α -Halonitrile-Stabilized Anions

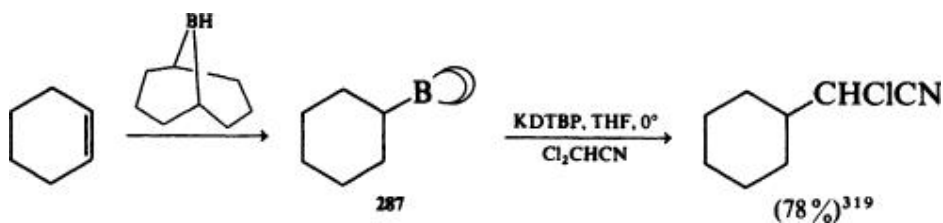
3.6.1.1. Alkylation

The direct alkylation of α -halonitriles with alkyl halides has not been investigated, with the possible exception of the dimerization of 2-bromo-2-phenylacetonitrile (**285**) to give dicyanostilbene (**286**). (79, 493-496)



Fortunately, a versatile indirect procedure is available for the alkylation or arylation of dichloroacetonitrile using organoboranes. (319) The addition of the anion of dichloroacetonitrile to a *B*-alkyl-9-borabicyclo [3, 3, 1]-nonane derivative such as **287** and subsequent migration of the *B*-alkyl group provides

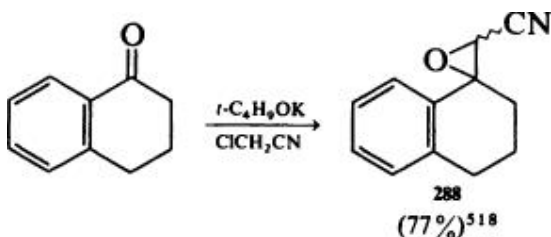
an efficient pathway for the formal alkylation of chloroacetonitrile with an array of olefins.



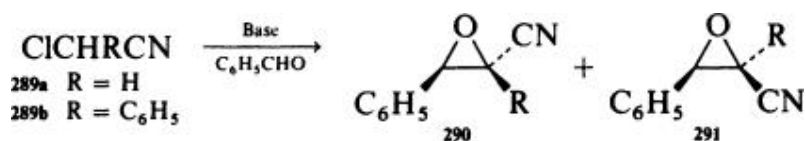
3.6.1.2. Addition to Aldehydes and Ketones

Extension of the Darzens glycidic ester synthesis (64, 497-499) to the synthesis of glycidonitriles involves the condensation of anions of α -halonitriles with carbonyl compounds to generate the intermediate halohydrins and the subsequent intramolecular displacement of the halide to generate the glycidonitriles. In general, the yields of glycidonitriles in reactions using various α -haloacetonitriles increase in the order $\text{I} < \text{Br} < \text{Cl}$. (500, 501) Competition experiments indicate that the reactivity of α -halonitriles and α -haloesters decreases in the order $\text{ClCH}_2\text{CO}_2\text{C}_2\text{H}_5 > \text{ClCH}_2\text{CN} > \text{FCH}_2\text{CO}_2\text{C}_2\text{H}_5$, (502) but this order does not reflect the superior yields often encountered in reactions of α -chloronitriles with aldehydes and, particularly, ketones in contrast to the reactions of their α -chloroester counter-parts.

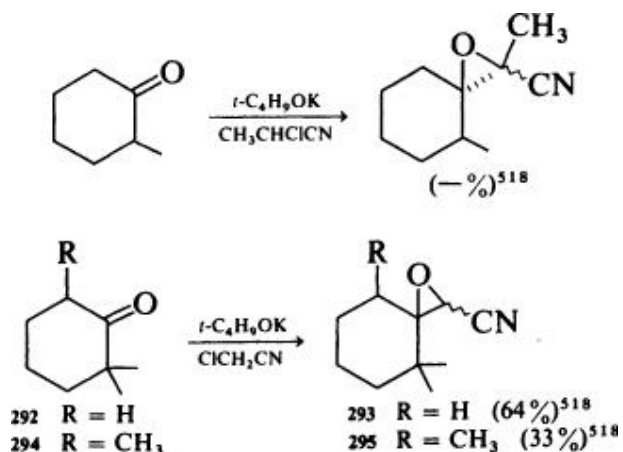
Typical bases used for the condensation include sodium hydride, (503-507) sodium hydroxide, (508) sodium methoxide, (509-511) sodium ethoxide, (502, 512-517) sodium or potassium *tert*-butoxide, (503, 504, 507, 518-520) sodium *tert*-amyloxide, (521-525) lithium, sodium or potassium amide, (503, 510, 519) and sodium bis(trimethylsilyl)amide (507) in a variety of solvents, including ether, benzene, *tert*-butyl alcohol, and hexamethylphosphoramide. Phase-transfer catalysis with the use of sodium hydroxide has also been employed in Darzens condensations. (526-531) In general, hindered alkoxide bases are preferred in the Darzens glycidonitrile synthesis, as illustrated in the preparation of 288, (518) in order to avoid the formation of iminoesters that are encountered using methoxide or ethoxide as bases. (123, 518)



The Darzens condensation of chloroacetonitrile (**289a**) with unsymmetrical carbonyl compounds exhibits relatively little stereoselectivity. In reactions with benzaldehyde (**504**, **505**, **532**) using sodium hydride as base, the *E/Z* ratio of glycidonitriles **290a** and **291a** varies from only 1.6 in 1,2-dimethoxyethane to 1.0 in hexamethylphosphoramide. (**505**) Similar limited variation in diastereomer ratios is noted in condensations with acetophenone. (**503**) In marked contrast, the condensation of 2-chloro-2-phenylacetonitrile (**289b**) with benzaldehyde (**529**, **533**) exhibits a substantial variation in stereoselectivity depending on the reaction conditions. With the use of sodium *tert*-butoxide, for example, the *E/Z* ratio of glycidonitriles **290b** and **291b** varies from 5.7 in benzene to 0.02 in hexamethylphosphoramide. (**533**)

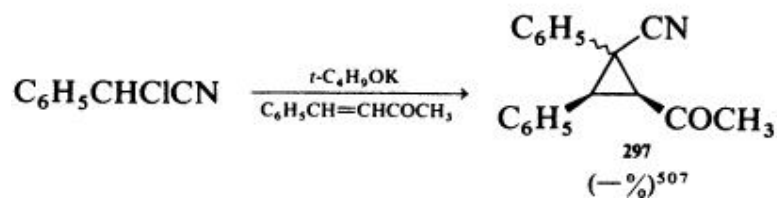
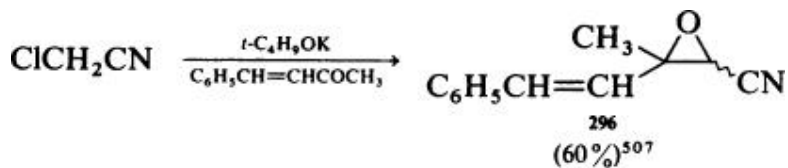


In substituted cyclohexanones, equatorial attack by the anion of chloroacetonitrile furnishes diastereomers bearing an axial carbon-oxygen epoxide bond. (**518**) In addition, the small size of the nitrile group allows the condensation of chloroacetonitrile with 2,2-dimethylcyclohexanone (**292**) or 2,2,6-trimethyl-cyclohexanone (**294**) to give the glycidonitriles **293** and **295** in 64% and 33% yields, respectively. In contrast, methyl chloroacetate condenses with **292** in only 20% yield; moreover, it fails to condense with **294**. (**518**) The extended scope of the chloroacetonitrile Darzens condensations relative to their carboxylic ester counterparts and the stereoselectivity observed in condensations of unsymmetrical cyclic ketones make the glycidonitrile synthesis an attractive reaction. Furthermore, glycidonitriles are conveniently transformed to a variety of other products, including α -chloroketones and α -fluoroketones, (**518**) unsaturated ketones and aldehydes, (**518**) 1,3-aminoalcohols, (**518**) and indoles. (**515**) Hydrolysis of glycidonitriles also provides a one-carbon homologation procedure for the conversion of carbonyl compounds to aldehydes (**514**) or carboxylic acids. (**521**)



3.6.1.3. Addition to Various Michael Acceptors

The condensation of the highly nucleophilic anion of chloroacetonitrile with unsaturated carbonyl compounds proceeds in a 1,2 fashion with 4-phenyl-3-buten-2-one to give the unsaturated glycidonitrile **296** as a mixture of diastereomers. In contrast, the anion of 2-chloro-2-phenylacetonitrile attacks 4-phenyl-3-buten-2-one in a 1,4 sense to give the cyclopropane derivatives **297**. (507)



4. Experimental Conditions and Procedures

On the basis of an overview of the tabulated reactions, the most useful bases for the alkylation, arylation, and acylation of nitriles would appear to be the alkali metal hydrides, amides, and dialkylamides. These bases require anhydrous solvents and an element of experimental caution but offer the best yields for the broadest array of electrophiles. The most notable exception to this generalization is the sodium hydroxide-promoted alkylation and arylation of arylacetonitriles under phase-transfer conditions.

Reactions of primary nitriles with various electrophiles under conditions designed to give monoalkylation are inevitably accompanied by the dialkylated byproduct as well as unalkylated starting material. The use of an excess of the nitrile starting material obviously reduces the amount of the dialkylated byproduct and provides an acceptable route to the monoalkylated product, provided the unalkylated material is recovered or removed from the product mixture. In many cases where the nitrile component is the most precious component, this solution is clearly unsatisfactory. In such cases separation of the desired monoalkylated product requires chromatography or distillation, but distillation of such mixtures finds useful application only when the electrophilic component adds a significant increment to the molecular weight of the product. In cases where the scale of the reaction prohibits chromatography or where the electrophile has three or fewer carbons, separation schemes are available that involve either the condensation of the mixture with benzaldehyde for removal of the unalkylated material or the selective saponification of the least-hindered components of the mixture for removal of the dialkylated byproduct. These schemes are not without obvious defects, and hence the alternative condensation–reduction approaches are preferred where the direct monoalkylation procedures provide intractable mixtures. An alternative involves the alkylation of a substituted cyanoacetate and subsequent decarboxylation to obtain the desired secondary nitrile. (131, 534)

The acylation of nitriles furnishes a product considerably more acidic than the starting material. One consequence of this observation is the reduced nucleophilicity of the acylated product relative to the nitrile starting material. Diacylation is rarely a problem, and, in addition, monoacylation provides yet another solution to the problem of the monoalkylation of primary nitriles. The acylation of primary nitriles with alkyl chloroformates or dialkyl carbonates and the subsequent alkylation–decarboxylation excludes the production of any dialkylated material, but, in practice, the yield in such a three-step process probably does not compete with the direct alkylation of the primary nitrile.

The following examples serve to illustrate the range of bases and electrophiles

that react successfully with various nitrile-stabilized carbanions. Since lithium diisopropylamide, lithium diethylamide, and sodium bis(trimethylsilyl)-amide are commonly used for the generation of nitrile anions, procedures for their preparation are included.

4.1.1.1. Lithium Diisopropylamide (LDA) 535a

After 22.8 mL of a hexane solution containing 34.2 mmol of *n*-butyllithium was diluted with 30 mL of anhydrous pentane, 4.15 g (41.5 mmol) of diisopropylamine was added dropwise and with stirring over a 45-minute period. Titration (536) of the resulting colorless solution of LDA with a 2,2'-bipyridyl indicator showed the concentration of the amide to be 0.53 M; at the end point of this titration, the color of the solution changed from dark brown to pale yellow green. Such solutions of LDA in pentane–hexane mixtures were stable for weeks at 25° provided they were not cooled or concentrated to induce the irreversible separation of solid LDA.

4.1.1.2. Lithium Diethylamide 535b

To 60 mL (0.051 mol) of *n*-butyllithium in ether at –15° under nitrogen was added 5.2 mL (0.051 mol) of anhydrous diethylamine in 25 mL of ether. The solution was stirred for 15 minutes at –15° to obtain a 0.565 M solution of lithium diethylamide. Alternative procedures use phenyllithium 535c or lithium metal 535b in place of *n*-butyllithium.

4.1.1.3. Sodium Bis(trimethylsilyl)amide 535e

A mixture of 81 g (0.55 mol) of hexamethyldisilazane and 65 g of a 30% sodium amide-benzene suspension in an additional 150 mL of benzene was heated at reflux under a nitrogen stream. The solution of sodium bis(trimethylsilyl)amide was used directly, or alternatively, white crystalline sodium bis(trimethylsilyl)amide was obtained after filtration and concentration in practically quantitative yield.

4.1.1.4. 2-Cyclopentyl-3-phenylpropionitrile (537) [Alkylation of an Aralkyl Nitrile Using Lithium Isopropylcyclohexylamide (LICA)]

To a solution of 1.5 mmol of LICA in 2.2 mL of THF–hexane at –78° under a nitrogen atmosphere was added 197 mg (1.5 mmol) of 3-phenylpropionitrile in 0.4 mL of tetrahydrofuran. After stirring for 5 minutes, this solution was transferred by syringe to a solution of 234 mg (1.57 mmol, 1.05 eq) of cyclopentyl bromide in 0.4 mL of tetrahydrofuran at –78° under a nitrogen atmosphere. The solution was stirred for 1 hour at –78° and 1 hour at 25°. The product was poured into ether, washed with 5% aqueous hydrochloric acid and subsequently with brine, and dried over magnesium sulfate. Chromatography on silica gel furnished 227 mg (76%) of 2-cyclopentyl-3-phenylpropionitrile. Repetition of this experiment using 7.56 g of 3-phenylpropionitrile gave 5.83 g (51%) of product after fractional distillation, bp 114–116° (0.2 mm). Gas–liquid

chromatographic analysis (3 m, 5% SE-30 at 200°) showed that the product was pure.

4.1.1.5. 4-Trimethylsiloxyvaleronitrile (160, 180) [Alkylation of Acetonitrile with an Epoxide]

To a solution of 4.12 g (0.1 mol) of acetonitrile in 300 mL of tetrahydrofuran at -78° was added 0.1 mol of LDA in tetrahydrofuran followed by 5.94 g (0.102 mol) of propylene oxide. After stirring for 1.5 hours at 25° and 1 hour at 65° , the reaction was quenched with 16 g (0.149 mol) of chlorotrimethylsilane. The mixture was stirred for an additional 45 minutes at 25° , concentrated under reduced pressure, diluted with 100 mL of ether, filtered, and again concentrated. The crude product was distilled to afford 13.1 g (78%) of 4-trimethylsiloxyvaleronitrile, bp $65\text{--}67^{\circ}$ (3 mm).

4.1.1.6. 2,2,3-Triphenylpropionitrile [Alkylation of an Arylacetonitrile Using Potassium Amide]

The preparation of this compound in 95–99% yield by the alkylation of diphenylacetonitrile with benzyl chloride is described in *Organic Syntheses*. (538)

4.1.1.7. 2-Phenyl-4-methylvaleronitrile (539) [Alkylation of an Arylacetonitrile Using Sodium Hydride]

To a suspension of 24.4 g (1.017 mol) of sodium hydride in 200 mL of anhydrous toluene was added a mixture of 122 g (1.043 mol) of phenylacetonitrile and 150 g (1.095 mol) of isobutyl bromide. The mixture was heated at 65° , at which temperature the reaction commenced. The heating mantle was removed, and the flask was cooled in order to keep the reaction from becoming too vigorous during the initial 0.5-hour reaction period. The reaction mixture was refluxed for an additional 5 hours and permitted to stand overnight. Ethanol (40 mL) was cautiously added dropwise, followed by the dropwise addition of 200 mL of water. The organic layer was separated, and the aqueous layer was extracted with benzene. The combined organic layers were washed successively with dilute acid, water, sodium carbonate solution, and water. After filtration through a layer of sodium sulfate, the benzene was evaporated and the product was fractionally distilled to afford 115 g (66%) of 2-phenyl-4-methylvaleronitrile, bp $130\text{--}134^{\circ}$ (10 mm) [lit. (540) bp $136\text{--}138^{\circ}$ (15 mm)].

4.1.1.8. 2-Phenylbutyronitrile (85) [Alkylation of an Arylacetonitrile Using Phase-Transfer Catalysis]

To 540 mL of aqueous 50% sodium hydroxide, 257 g (253 mL, 2.2 mol) of phenylacetonitrile and 5.0 g (0.022 mol) of benzyltriethylammonium chloride was added 218 g (150 mL, 2 mol) of bromoethane dropwise over a period of approximately 100 minutes at $28\text{--}35^{\circ}$. After addition of bromoethane was complete, stirring was continued for 2 hours and then the temperature was

increased to 40° for an additional 30 minutes. The reaction mixture was cooled to 25°, and 21.2 g (20.3 mL, 0.2 mol) of benzaldehyde was added. The mixture was stirred for 1 hour; the flask was then immersed in a cold-water bath, and 750 mL of water and 100 mL of benzene were added. The layers were separated, and the aqueous phase was extracted with 200 mL of benzene. The organic layers were combined and washed successively with water, dilute hydrochloric acid, and water. The organic layer was dried over magnesium sulfate, and the solvent was removed by distillation under reduced pressure. The product was distilled through a Vigreux column to give 235–242 g (78–84%) of 2-phenylbutyronitrile, bp 102–104° (7 mm).

4.1.1.9. 3-Phenyl-5-chloroanthranil (154) [Arylation of an Arylacetonitrile]

To a solution of 74 g (1.1 mol) of potassium hydroxide in 150 mL of methanol was added with stirring and cooling in an ice bath 8.1 g (0.069 mol) of phenylacetonitrile and a solution of 9.9 g (0.063 mol) of 4-nitrochlorobenzene in 100 mL of methanol. The mixture was stirred for 4 hours at 0–5°, and then 400 mL of water was added with stirring. The precipitate was isolated by filtration, washed with water, and dried. Recrystallization from petroleum ether (bp 60–71°) afforded 6.7 g (46%) of pale yellow needles of 3-phenyl-5-chloroanthranil, mp 114–116°.

4.1.1.10. 2-(4-Nitrophenyl)-2-phenylpropionitrile (83) [Arylation of an Arylacetonitrile Involving Halogen Substitution]

To 6.55 g (0.05 mol) of 2-phenylpropionitrile, 7.88 g (0.05 mol) of 4-chloronitrobenzene, 0.23 g and (0.001 mol) of benzyltriethylammonium chloride in 5–10 mL of benzene or acetonitrile was added 10–15 mL of 50% aqueous sodium hydroxide in small portions. An external cooling bath was applied to maintain the reaction temperature in the 40–50° range. The mixture was stirred for an additional 3–4 hours at 40–50°, cooled, and diluted with water. The mixture was extracted with benzene, dried, and concentrated. Distillation of the crude product furnished 11.6 g (92%) of 2-(4-nitrophenyl)-2-phenylpropionitrile, bp 170° (0.3 mm), mp 76°.

4.1.1.11. 3-Ethoxy-2-methyl-2-phenyl-3-butenenitrile (88) [Vinylolation of an Arylacetonitrile]

To 3.3 g (0.025 mol) of 2-phenylpropionitrile and 2.1–3.5 g (0.03–0.05) mol of ethoxyacetylene in 5 mL of dimethyl sulfoxide under a nitrogen atmosphere was added 3 g of powdered potassium hydroxide or sodium hydroxide and 0.1 g of benzyltriethylammonium chloride. The mixture was allowed to stand in a closed vessel at ambient temperature for 24–36 hours. The product was extracted into benzene, washed with water, dried, and distilled to afford 3.2 g (64%) of 3-ethoxy-2-methyl-2-phenyl-3-butenenitrile, bp 134° (9 mm).

4.1.1.12. Ethyl 2-Cyanoctanoate (292) [Acylation of an Alkylacetonitrile]

To 3.1 g (46 mmol) of LDA in approximately 70 mL of a 40% hexane-tetrahydrofuran solution at -74° was added 2.5 g (20 mmol) of octanenitrile in 15 mL of tetrahydrofuran. The solution was stirred for 0.5 hour at -74° and 0.5 hour at 25° . To the nitrile anion solution that was recooled to -74° was added 2.48 g (21 mmol) of diethyl carbonate in 10 mL of tetrahydrofuran. The solution was stirred for 2.5 hours at -74° and quenched with 10 mL of saturated, aqueous ammonium chloride solution. The crude product was diluted with ether; washed successively with water, aqueous hydrochloric acid, and brine; dried; and distilled to afford 2.97 g (76%) of ethyl 2-cyanoctanoate, bp $69-71^{\circ}$ (0.04 mm).

4.1.1.13. *2-(4-Chlorophenyl)-4-phenyl-3-oxobutyronitrile*. [Acylation of an Arylacetonitrile]

The preparation of this compound in 74–82% yield by the condensation of 4-chlorophenylacetonitrile and ethyl phenylacetate is described in *Organic Syntheses*. (541)

4.1.1.14. *(Z)-2-(5-Benzyloxy-3-methyl-3-penten-1-yl)-3-hydroxy-4,4-dimethylvaleronitrile* (542) [Alkylation of an Alkylacetonitrile with an Aldehyde]

To a solution of 4 mmol of LDA in 7.5 mL of 45% hexane–tetrahydrofuran at -78° was added 458 mg (2 mmol) of (*Z*)-7-benzyloxy-5-methyl-5-heptenenitrile and 222 mg (2.6 mmol, 1.3 eq) of pivalaldehyde in 2 mL of tetrahydrofuran over 10 minutes. The reaction mixture was stirred at -78° under nitrogen for 4.5 hours, hydrolyzed by the addition of 3 mL of saturated ammonium chloride, and allowed to warm to room temperature. Water was added, and the product was extracted with three portions of ether. The ether solution was washed three times with 10% hydrochloric acid, three times with water, and once with saturated sodium chloride. After the ether solution was dried over magnesium sulfate and the solvent removed, the residue (0.85 g) was purified by chromatography on 90 g of silica gel. Elution with 10% acetone in hexane afforded 0.482 g (76%) of (*Z*)-2-(5-benzyloxy-3-methyl-3-penten-1-yl)-3-hydroxy-4,4-dimethylpentanenitrile.

4.1.1.15. *Dimethyl 4-(4-Chlorophenyl)-4-cyanopimelate* (383) [1,4 Addition of Arylacetonitrile to an Unsaturated Ester]

A mixture of 18.8 g (0.124 mol) of 4-chlorophenylacetonitrile and 58 mL of methyl acrylate in 60 mL of *tert*-butyl alcohol was brought to reflux temperature. Heating was discontinued, and 10 mL of 40% methanolic Triton B in 28 mL of *tert*-butyl alcohol was added quickly. After 4 hours at the reflux temperature, the mixture was allowed to cool and was subsequently shaken with water and benzene. The organic layer was washed successively with 2.5 *N* hydrochloric acid solution and brine, and the solvent was evaporated. The residue was distilled to afford 28.4 g (71%) of dimethyl 4-(4-chlorophenyl)-4-cyanopimelate, bp $186-191^{\circ}$ (0.35 mm).

4.1.1.16. *Cyclopropyl Cyanide [Intramolecular Alkylation of an Alkylacetonitrile]*

The preparation of this compound in 52–53% yield by the alkylation of 4-chlorobutanenitrile with the use of sodium amide is described in *Organic Syntheses*. (543)

4.1.1.17. *1-Cyanobenzocyclobutene [Intramolecular Arylation of an Alkyl nitrile]*

The preparation of this compound in 64–66% yield by the intramolecular arylation of 3-(2-chlorophenyl)propanenitrile is described in *Organic Syntheses*. (274)

4.1.1.18. *10-Cyano-1,3,8-trimethoxyanthracen-9-ol (269) [Intramolecular Arylation of an Arylacetonitrile]*

Sodium methoxide (75 mg, 1.8 mmol) was added under nitrogen to a stirred solution of 2-cyanomethyl-2,4,6,6-tetramethoxybenzophenone (340 mg, 1 mmol) in 20 mL of anhydrous dimethyl sulfoxide. The resulting red solution was heated to 140° and maintained at this temperature for 100 minutes. The solution was cooled, poured into 200 mL of cold 1 M hydrochloric acid solution, and extracted with chloroform. The combined organic phase was washed with water and dried, and the solvent was removed to give a yellow crystalline residue. Recrystallization from ethyl acetate gave 280 mg (94%) of 10-cyano-1,3,8-trimethoxyanthracen-9-ol as yellow needles, mp 252°.

4.1.1.19. *2-Cyanobenzyl Phenyl Ketone (405) [Acylation of an Unsaturated Nitrile]*

To a rapidly stirred solution of potassium amide prepared from potassium metal (0.1 g-atom, 3.8 g) in 150 mL of anhydrous liquid ammonia was added 11.7 g of 2-tolunitrile in 25 mL of anhydrous ether. An intense red color developed immediately, and the reaction mixture was stirred for an additional 10 minutes to ensure the conversion of the nitrile to its anion. Methyl benzoate (6.8 g, 0.05 mol) in 25 mL of anhydrous ether was added over 10 minutes, at which time the color of the reaction mixture had turned from red to green. Stirring was continued for an additional 1 hour, and the reaction was quenched by the addition of ammonium chloride (6.1 g). The liquid ammonia was displaced by adding 150 mL of ether and heating on a steam bath until the ether began to reflux. The reaction mixture was then poured into a water–ice slurry and acidified with 6 N hydrochloric acid. The phases were separated, and the aqueous phase was extracted with several portions of chloroform. The combined ether and chloroform phases were dried over sodium sulfate, concentrated, and distilled to give 7.3 g (66%) of 2-cyanobenzyl phenyl ketone, mp 109.1–109.8°.

4.1.1.20. *2-Ethoxy-2-phenylbutyronitrile (424) [Alkylation of a Protected Cyanohydrin]*

A solution of potassium *tert*-butoxide (27 g, 0.24 mol) in 270 mL of dry tetrahydrofuran was added dropwise over 30 minutes under nitrogen to a solution of 2-ethoxy-2-phenylacetonitrile (32.2 g, 0.2 mol) in 100 mL of tetrahydrofuran. After an additional 15 minutes 39 g (0.25 mol) of ethyl iodide was added over 15 minutes. The temperature was allowed to warm to 15–20° during the addition of the halide, and the reaction was maintained at this temperature for an additional 45 minutes. The mixture was filtered, and the filtrate was distilled to give 23.8 g (63%) of 2-ethoxy-2-phenylbutyronitrile, bp 113–114° (12 mm).

4.1.1.21. 3-(4-Chlorobenzoyl)propionitrile (440) [1,4 Addition of a Cyanohydrin to an Unsaturated Nitrile]

To a solution of 200 mL of dimethylformamide and 1.0 g (0.02 mol) of sodium cyanide was added a solution of 56.2 g (0.4 mol) of 4-chlorobenzaldehyde in 120 mL of dimethylformamide dropwise over 45 minutes at 35° to obtain a creamy product. Stirring was then continued for 15 minutes, and a solution of 15.9 g (0.3 mol) of freshly distilled acrylonitrile in 80 mL of dimethylformamide was added to this reaction mixture dropwise in the course of 1.5 hours at 34–35°. Stirring was continued for 1.5 hours at the same temperature. A very creamy product was again formed toward the end of the reaction. About 1 L of water was added to the reaction mixture, and the mixture was shaken vigorously. The reaction product was extracted with chloroform. The chloroform solution was washed with water, dried over magnesium sulfate, and the solvent was removed. The crude product (67.9 g) (88%) was distilled to afford 3-(4-chlorobenzoyl)propionitrile, bp 178–182° (0.5 mm), mp 72–73° (lit. (544) mp 76°).

4.1.1.22. 2-Diethylcarbamoylthioheptanenitrile (457) [Alkylation of an α -Sulfur-Substituted Nitrile]

To 0.86 g (5 mmol) of *S*-cyanomethyl diethylthiocarbamate and 92 mg (0.25 mmol, 0.05 eq.) of tetrabutylammonium iodide in 5 mL of 50% aqueous sodium hydroxide was added 0.62 mL (5 mmol) of 1-bromopentane. The solution was vigorously stirred for 10 hours, diluted with 20 mL of water, and extracted with two 20-mL portions of ether. The ether solution was washed successively with three 20-mL portions of water and 20 mL of brine and dried over sodium sulfate. The crude product was purified by column chromatography with alumina and eluting with 4:1 hexane–chloroform to afford 1.16 g (95%) of 2-diethylcarbamoylthioheptanenitrile.

4.1.1.23. 2-Methyl-3-pyridyl 2-Cyanoethyl Ketone (488) [[2,3]-Sigmatropic Rearrangement of an Ammonium Ylid Bearing Nitrile Functionality]

A solution of 12.32 g (35.6 mmol) of 1-cyanomethyl-1-(2-picoyl)pyrrolidinium benzenesulfonate in 125 mL of anhydrous dimethyl sulfoxide and 290 mL of anhydrous tetrahydrofuran was cooled to –10°, and 1.84 g (38.1 mmol) of 50% sodium hydride in mineral oil was added. The mixture was stirred at –5° to

–10° for 0.5 hour and allowed to warm to room temperature over 1.5 hours. An additional 1.84 g (38.1 mmol) of 50% sodium hydride in mineral oil was added, and the mixture was heated under reflux for 0.5 hour and then cooled to –10°. A solution of 5.1 g (38 mmol) of 3-bromopropionitrile in 25 mL of tetrahydrofuran was added over 0.5 hour and the reaction stirred for an additional 0.5 hour. The reaction mixture was filtered and concentrated under reduced pressure. The residue was dissolved in ether, and the ethereal solution was washed with a saturated sodium chloride–potassium carbonate solution. The organic solution was filtered, dried over sodium sulfate, and evaporated to give 8.17 g of brown oil. To the oil was added 5 mL of tetrahydrofuran, 15 mL of water, and 30 mL of acetic acid. The solution was stirred at 53° for 24 hours; the volume was reduced to 20 mL under reduced pressure and the product was acidified with 40 mL of 2.2 *N* hydrochloric acid. The aqueous solution was washed with two portions of ether, basified with potassium carbonate, and extracted with methylene chloride. The methylene chloride solution was dried over magnesium sulfate and the solvent was removed *in vacuo*. The residue was distilled [147° (0.1 mm)] to yield a yellow oil that crystallized on trituration with ether. The colorless crystals were collected and dried. The yield of 2-methyl-3-pyridyl 2-cyanoethyl ketone was 3.2 g (53%), mp 82–83.5°.

5. Tabular Survey of the Reactions of Nitrile Anions

The tables are arranged according to the nature of the nitrile anion and the electrophile. The nitriles are arbitrarily divided into six broad families: (1) simple alkyl, aryl, and heteroaryl nitriles; (2) α , β -unsaturated and β , γ -unsaturated nitriles as well as tolunitriles; (3) cyanohydrins and their hydroxylprotected derivatives; (4) protected thiocyanohydrins; (5) α -(dialkylamino)-nitriles; and (6) α -halonitriles. Within each of these families, various tables are assembled to cover (1) alkylation reactions with alkyl halides, alkyl sulfonates, epoxides, and aziridines; (2) arylation reactions; (3) acylations with carboxylic acid chlorides, anhydrides, esters, nitriles, and dialkyl carbonates; (4) addition reactions with aldehydes, ketones, imines, alkenes, and alkynes; (5) addition reactions to various unsaturated Michael acceptors, and finally (6) intramolecular reactions involving alkylations, acylations, arylation, and Michael-type additions. The intramolecular cases include dialkylation reactions where only one of the two alkylation steps involves an intramolecular reaction. The α , β -unsaturated or β , γ -unsaturated nitriles that also bear various α -oxygen, α -sulfur, α -dialkylamino, or α -halo substituents are listed in the tables corresponding to the various α substituents. Within each table, the compounds are listed in order of increasing number of carbon atoms monoalkylated derivatives listed before dialkylated derivatives, and acyclic groups are listed first followed by monocyclic, aromatic, and heterocyclic substituents. The straight-chain alkyl derivatives are placed before the branched-chain derivatives; the latter groups are listed in order of increased branching. Monocyclic derivatives precede bicyclic derivatives with the isomers with the smallest ring listed first. Oxygen heterocycles are found before sulfur heterocycles, which, in turn, precede nitrogen heterocycles.

The electrophilic agents are also arranged in order of increasing number of carbons. Within a group of electrophilic agents with the same number of carbons, the order of arrangement is chlorides, bromides, iodides, unsaturated halides, sulfonates, epoxides, dihalides, and carbonates. Remaining cases are listed in order of increasing unsaturation. Analogs of these electrophilic agents having heteroatoms inserted in the ring or chain follow the carbocyclic parent to which they are most closely related and following an order in which oxygen precedes sulfur and sulfur precedes nitrogen.

In those entries where more than one reference is cited, the experimental data are taken from the first reference. In examples where the isolated compound resulted from the transformation of the initial adduct, the yield refers to the isolated product, and the footnote denotes the nature of the transformation. The literature is reviewed from 1952 (1) through February 1982. The absence of a rigorous method for gathering all examples of the reactions under review

has undoubtedly resulted in certain omissions for which the authors apologize. Credit for the successful compilation of references and completion of this review goes in part to Beryl Dominy of Pfizer, Thomas Johns of DuPont, and Linda Keiter of the University of Wyoming Science Library to whom the authors are indebted.

Standard abbreviations used throughout the tables are as follows:

B	9-borabicyclononyl
$\text{C}_4\text{H}_3\text{O}$	furyl
$\text{C}_4\text{H}_3\text{S}$	thienyl
$\text{C}_5\text{H}_4\text{N}$	pyridyl
C_6H_{11}	cyclohexyl
C_{10}H_7	naphthyl
$\text{C}_{10}\text{H}_8\text{Mg}$	magnesium naphthalide
$\text{C}_{10}\text{H}_8\text{Na}$	sodium naphthalide
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
Et_2O	diethyl ether
e^-	electrolysis
Fc	ferrocenyl
$(\text{HCHO})_n$	paraformaldehyde
HMPA	hexamethylphosphoramide
KDTBP	potassium 2,6-di- <i>tert</i> -butylphenoxide
K_xC_y	potassium graphite
LDA	lithium diisopropylamide
LICA	lithium isopropylcyclohexylamide
LTMP	lithium tetramethylpiperidide
Py	pyridine
P	polystyrene
THF	tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine

Table I. Alkylation of Nitrile-Stabilized Carbanions with Alkyl Halides, Alkyl Sulfonates, Epoxides, and Aziridines

[View PDF](#)

Table II. Arylation of Nitrile-Stabilized Carbanions

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Table III. Acylation of Nitrile-Stabilized Carbanions with Carboxylic Esters, Anhydrides, Acid Chlorides, Nitriles, and Dialkyl Carbonates

[View PDF](#)

Table IV. Addition of Nitrile-Stabilized Carbanions to Aldehydes, Ketones, Imines, Alkenes, and Alkynes

[View PDF](#)

Table V. Tandem Conjugate Addition–Alkylation of α , β -Unsaturated Nitriles with Carbonyl Compounds

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Table VI. 1,2-Addition and 1,4-Addition Reactions of Nitrile-Stabilized Carbanions to Various Michael Acceptors

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Table VII. Intramolecular Reactions of Nitrile-Stabilized Carbanions

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Table VIII. Alkylation of Unsaturated Nitriles with Alkyl Halides

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Table IX. Acylation of Unsaturated Nitrile-Stabilized Carbanions with Carboxylic Esters and Nitriles

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Table X. Addition of Unsaturated Nitrile-Stabilized Carbanions to Aldehydes, Ketones, and Various Michael Acceptors

[View PDF](#)

Table XI. Intramolecular Reactions of Unsaturated Nitrile-Stabilized Carbanions

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Table XII. Alkylation of Anions of Protected Cyanohydrins with Alkyl Halides

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Table XIII. Arylation of Protected Cyanohydrins

[View PDF](#)

Table XIV. Acylation of Anions of Protected Cyanohydrins

[View PDF](#)

Table XV. Addition of Anions of Protected Cyanohydrins to Aldehydes, Ketones, and Olefins

[View PDF](#)

Table XVI. 1,2-Addition and 1,4-Addition Reactions of Anions of Protected Cyanohydrins to Various Michael Acceptors

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**Table XVII. Intramolecular Reactions of Anions of Protected
Cyanohydrins**

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**Table XVIII. Alkylation of Nitrile-Stabilized Carbanions Bearing α -Sulfur
or α -Selenium Substituents**

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**Table XIX. Arylation of Nitrile-Stabilized Carbanions Bearing α -Sulfur
Substituents**

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**Table XX. Addition of Nitrile-Stabilized Carbanions Bearing α -Sulfur
Substituents to Aldehydes and Ketones**

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**Table XXI. 1,2 Addition and 1,4 Addition of Nitrile-Stabilized Carbanions
Bearing α -Sulfur Substituents to Various Michael Acceptors**

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Table XXII. Intramolecular Reactions of Nitrile-Stabilized Carbanions Bearing α -Sulfur Substituents

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Table XXIII. Alkylation of α -(Dialkylamino)nitrile-Stabilized Carbanions with Alkyl Halides and Epoxides

[View PDF](#)

Table XXIV. Tandem Conjugate Addition–Alkylation of α -(Dialkylamino)acrylonitriles with Alkyl Halides

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Table XXV. Arylation of α -(Dialkylamino)nitrile-Stabilized Carbanions

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Table XXVI. Acylation of α -(Dialkylamino)nitrile-Stabilized Carbanions

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Table XXVII. Addition of α -(Dialkylamino)nitrile-Stabilized Carbanions to Aldehydes and Ketones

[View PDF](#)

Table XXVIII. 1,2 Addition and 1,4 Addition of α -(Dialkylamino)nitrile-Stabilized Carbanions to Various Michael Acceptors

[View PDF](#)

Table XXIX. Intramolecular Reactions of α -(Dialkylamino)nitrile-Stabilized Carbanions or Tetraalkylammonium Ylids

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Table XXX. Alkylation of α -Halonnitrile-Stabilized Carbanions

[View PDF](#)

Table XXXI. Arylation of α -Halonnitrile-Stabilized Carbanions

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Table XXXII. Darzens Glycidonitrile Synthesis: Reactions of α -Halonnitrile-Stabilized Carbanions with Aldehydes and Ketones

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
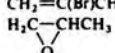
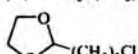

Table XXXIII. Tandem Conjugate Addition–Alkylation of α -Haloacrylonitriles

[View PDF](#)

Table XXXIV. Intramolecular Reactions of α -Halonitrile-Stabilized Anions

[View PDF](#)

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₂	CH ₃ CN	CH ₃ I	NaN[Si(CH ₃) ₂] ₂
		C ₂ H ₅ Br	C ₁₀ H ₈ Na
			NaNH ₂
		"	LDA
		"	NaNH ₂
		ClCH ₂ CO ₂ Na	"
		<i>n</i> -C ₃ H ₇ Br*	Li, (C ₂ H ₅) ₂ NH
		Cl(CH ₂) ₂ Br	"
		"	LiN(C ₂ H ₅) ₂
		<i>i</i> -C ₃ H ₇ I	NaNH ₂
		CH ₂ =C(Br)CH ₂ Br	<i>n</i> -C ₄ H ₉ Li, -78°, CuI, -25°
			LDA
		"	NaNH ₂
		<i>n</i> -C ₄ H ₉ Br	<i>t</i> -C ₄ H ₉ Li
		"	C ₁₀ H ₈ Na
		Cl(CH ₂) ₆ Br	LiN(C ₂ H ₅) ₂
		CH ₂ =C(CH ₂ Br)CO ₂ C ₂ H ₅	<i>n</i> -C ₄ H ₉ Li, -78°, CuI, -25°
		<i>n</i> -C ₃ H ₇ Br	e ⁻ (8-10 V)
		Br(CH ₂) ₂ Br	NaNH ₂
		C ₂ H ₅ OSi(CH ₃) ₂ CH ₂ Br	NaN[Si(CH ₃) ₂] ₂
		(CH ₃ O) ₂ CH(CH ₂) ₂ Cl	NaNH ₂
		(<i>E</i>)-BrCH ₂ C(CH ₃)=CHCO ₂ CH ₃	<i>n</i> -C ₄ H ₉ Li, -78°, CuI, -25°
			NaNH ₂
		<i>n</i> -C ₆ H ₁₃ Br	e ⁻ (8-10 V)
			LDA
		<i>n</i> -C ₇ H ₁₅ Br	LiN(C ₂ H ₅) ₂
		"	K
Cl(CH ₂) ₆ CN	NaNH ₂		
(C ₂ H ₅ O) ₂ CH(CH ₂) ₂ Cl	"		
C ₆ H ₅ CH ₂ Cl	K ₂ C ₇		
"	<i>t</i> -C ₄ H ₉ Li		
C ₆ H ₅ CH ₂ Br	C ₁₀ H ₈ Na		
<i>n</i> -C ₈ H ₁₇ Br	K ₂ C ₇		
"	K, Al ₂ O ₃		
<i>n</i> -C ₈ H ₁₇ CHBrCH ₃	K ₂ C ₇		
(<i>i</i> -C ₃ H ₇ O) ₂ CH(CH ₂) ₂ Cl	NaNH ₂		
<i>trans</i> -Geranyl bromide	<i>n</i> -C ₄ H ₉ Li, -78°, CuI, -25°		
(<i>E</i>)- <i>n</i> -C ₇ H ₁₅ Cl=CHCH ₂ Br	"		
C ₂ H ₅ Br	<i>i</i> -C ₃ H ₇ MgCl		
"	NaNH ₂		
"	KNH ₂		
C ₂ H ₅ I, (1.5 eq)	<i>i</i> -C ₃ H ₇ MgCl (1.0 eq)		
C ₂ H ₅ I, (2.5 eq)	<i>i</i> -C ₃ H ₇ MgCl (2.0 eq)		
ClCH ₂ CO ₂ Na	NaNH ₂		
<i>i</i> -C ₃ H ₇ Br	Li, (C ₂ H ₅) ₂ NH		
<i>i</i> -C ₃ H ₇ I	NaNH ₂		
<i>n</i> -C ₄ H ₉ Br	NaH		
C ₂ H ₅ OSi(CH ₃) ₂ CH ₂ Br	NaN[Si(CH ₃) ₂] ₂		

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES

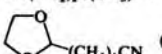
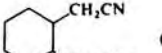
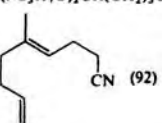
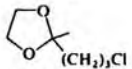
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₂ O	<i>t</i> -C ₄ H ₉ CN (-)	104
THF	<i>n</i> -C ₃ H ₇ CN (35)	198
Et ₂ O	(C ₂ H ₅) ₂ CCN (58)	545
"	(CH ₃) ₂ SiO(CH ₂) ₂ CN (68)*	160
THF, -30°	HOCH ₂ (CH ₂) ₂ CN (-)	159
NH ₃	HO ₂ C(CH ₂) ₂ CO ₂ H (-)*	546
C ₆ H ₆ , HMPA, -60°	(<i>n</i> -C ₃ H ₇) ₂ CCN (95)	547
"	Cl(CH ₂) ₆ CN (60)	548
HMPA	Cl(CH ₂) ₄ CN (70)	193
NH ₃	(<i>i</i> -C ₃ H ₇) ₂ CCN (18), (<i>i</i> -C ₃ H ₇) ₂ C=C=NC ₃ H ₇ - <i>i</i> (14)*	255
"	CH ₂ =C(Br)(CH ₂) ₂ CN (92)	48
"	(CH ₃) ₂ SiOCH(CH ₃)(CH ₂) ₂ CN (78)*	180,160
THF, -30°	HOCH(CH ₃)(CH ₂) ₂ CN (-)	159
Et ₂ O, THF, -78°	(<i>n</i> -C ₄ H ₉) ₂ CCN (-)	19
THF	<i>n</i> -C ₃ H ₇ CN (56)	198
Et ₂ O	Cl(CH ₂) ₂ CN (-)	549
"	CH ₂ =C(CO ₂ C ₂ H ₅)(CH ₂) ₂ CN (89)	48
"	<i>n</i> -C ₆ H ₁₃ CN (42)	113
NH ₃ , -65°	NC(CH ₂) ₂ CN (60-70)	209
C ₆ H ₆ , toluene	C ₂ H ₅ OSi(CH ₃) ₂ (CH ₂) ₂ CN (-)	218
NH ₃ , -40 to -60°	(CH ₃ O) ₂ CH(CH ₂) ₂ CN (51)	550
"	NC(CH ₂) ₂ C(CH ₃)=CHCO ₂ CH ₃ <i>E</i> (21), <i>Z</i> (46)	48
NH ₃ , -40 to -60°	 (-)	550
"	<i>n</i> -C ₇ H ₁₅ CN (41)	113
"	 (75)*	160
HMPA, -70°	<i>n</i> -C ₄ H ₉ CN (64), (<i>n</i> -C ₇ H ₁₅) ₂ CHCN (16)	361
HMPA	<i>n</i> -C ₄ H ₉ CN (-), (<i>n</i> -C ₇ H ₁₅) ₂ CHCN (-)	551
NH ₃ , -50°	NC(CH ₂) ₂ CN (80)	209
NH ₃ , -40 to -60°	(C ₂ H ₅ O) ₂ CH(CH ₂) ₂ CN (75)	550
THF, -60°	C ₆ H ₅ (CH ₂) ₂ CN (42)	552
Et ₂ O, THF, -78	(C ₆ H ₅ CH ₂) ₂ CCN (30)	19
THF	(C ₆ H ₅ CH ₂) ₂ CHCN (9), (C ₆ H ₅ CH ₂) ₂ CCN (26)	198
THF, -60°	<i>n</i> -C ₆ H ₁₃ CN (55), (<i>n</i> -C ₈ H ₁₇) ₂ CHCN (7)	552
"	<i>n</i> -C ₆ H ₁₃ CN (54)	553
"	<i>n</i> -C ₈ H ₁₇ CH(CH ₃)CH ₂ CN (25)	552
NH ₃ , -73 to -75°	(<i>i</i> -C ₃ H ₇ O) ₂ CH(CH ₂) ₂ CN (59)	550
-	 (92)	48
-	(<i>E</i>)- <i>n</i> -C ₇ H ₁₅ Cl=CH(CH ₂) ₂ CN (89)	48
HMPA, 85°	CH ₃ CH(C ₂ H ₅)CN I (62), CH ₃ C(C ₂ H ₅) ₂ CN II (20)	31
"	I (30-36), II (12)	554
NH ₃ , Et ₂ O	II (57)	555
HMPA, 85°	I (60), II (8)	31
"	I (6), II (81)	31
NH ₃	HO ₂ CCH ₂ CH(CH ₃)CO ₂ H (-)*	546
C ₆ H ₆ , HMPA, -60°	(<i>i</i> -C ₃ H ₇) ₂ C(CH ₃)CN (65)	547
NH ₃	" (59)	255
Toluene	<i>n</i> -C ₂ H ₅ CH(CH ₃)CN (23)	42
C ₆ H ₆ , toluene	C ₂ H ₅ OSi(CH ₃) ₂ CH ₂ CH(CH ₃)CN (-)	68

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₃ (Contd.)	C ₂ H ₅ CN	(CH ₃) ₂ C=CH(CH ₂) ₂ Br	Li(C ₂ H ₅) ₂
		C ₆ H ₅ CH ₂ Cl	LICA
			Li(C ₂ H ₅) ₂
		C ₆ H ₅ (CH ₂) ₃ Br	LICA
		C ₂ H ₅ OSO ₂ C ₆ H ₄ CH ₃ -4	<i>i</i> -C ₃ H ₇ MgCl
		C ₆ H ₅ (CH ₂) ₄ Br	LICA
		C ₆ H ₅ (CH ₂) ₂ CH(CH ₃)Br	"
		C ₂ H ₅ Br	NaNH ₂
		"	KNH ₂
		C ₂ H ₅ I	NaNH ₂
C ₄	<i>n</i> -C ₃ H ₇ CN	C ₂ H ₅ Br	NaNH ₂
		"	KNH ₂
		C ₂ H ₅ I	NaNH ₂
		"	<i>i</i> -C ₃ H ₇ MgCl
		"	"
		C ₂ H ₅ OSO ₂ C ₆ H ₄ CH ₃ -4	KNH ₂
		C ₂ H ₅ Br	Li, (C ₂ H ₅) ₂ NH
		Cl(CH ₂) ₃ Br	Li(C ₂ H ₅) ₂
		"	NaNH ₂
		<i>i</i> -C ₃ H ₇ Br	Li, (C ₂ H ₅) ₂ NH
	<i>i</i> -C ₃ H ₇ CN	<i>i</i> -C ₃ H ₇ I	Li(C ₂ H ₅) ₂
		Cl(CH ₂) ₃ Br	Li, (C ₂ H ₅) ₂ NH
		"	Li(C ₂ H ₅) ₂
		<i>i</i> -C ₃ H ₇ Br	Li, (C ₂ H ₅) ₂ NH
		<i>n</i> -C ₄ H ₉ Br	K ₂ C ₈
		"	KNH ₂
		<i>n</i> -C ₄ H ₉ I	Li(C ₂ H ₅) ₂
		(C ₂ H ₅) ₂ SO ₄	<i>i</i> -C ₃ H ₇ MgCl
		"	NaNH ₂
		<i>i</i> -C ₃ H ₇ CN	Li(C ₂ H ₅) ₂
<i>i</i> -C ₃ H ₇ CN	<i>n</i> -C ₄ H ₉ I	Li, (C ₂ H ₅) ₂ NH	
	<i>n</i> -C ₄ H ₉ Br	"	
	X(CH ₂) ₄ Br	"	
	Cl(CH ₂) ₄ Br	Li(C ₂ H ₅) ₂	
	ClCH ₂ CH(CH ₃)CH ₂ Br	Li, (C ₂ H ₅) ₂ NH	
	"	"	
	<i>n</i> -C ₄ H ₉ Br	NaNH ₂	
	<i>sec</i> -C ₅ H ₁₁ Br	Li, (C ₂ H ₅) ₂ NH	
	(CH ₃) ₂ C=CHCH ₂ Br	Li(C ₂ H ₅) ₂	
	"	(C ₂ H ₅) ₂ NMgBr	
<i>n</i> -C ₃ H ₇ CN	(CH ₃) ₂ C(CH ₂ Br) ₂	Li, (C ₂ H ₅) ₂ NH	
	(C ₂ H ₅ O) ₂ CHCH ₂ Br	LICA	
	CH ₂ C(OCH ₃) ₂ CH(CH ₃)Br	LDA	
	(C ₂ H ₅ O) ₂ CHCH ₂ Br	Li, (C ₂ H ₅) ₂ NH	
	[BrCH ₂ Si(CH ₃) ₂] ₂ O	NaN[Si(CH ₃) ₂] ₂	
	C ₆ H ₁₁ Br	NaNH ₂	
	<i>n</i> -C ₇ H ₁₅ Br	Li(C ₂ H ₅) ₂	
	<i>n</i> -C ₈ H ₁₇ Br	K, AlO ₃	
	"	LICA, (1.0 eq)	
	"	LICA, (2.0 eq)	
<i>i</i> -C ₃ H ₇ CN	"	KNH ₂	
	3,4-(CH ₂ O) ₂ C ₆ H ₃ CH ₂ Br	LDA	
	C ₆ H ₅ O(CH ₂) ₂ Br	Li(C ₂ H ₅) ₂	
	C ₂ H ₅ OSO ₂ C ₆ H ₄ CH ₃ -4	<i>i</i> -C ₃ H ₇ MgCl	
	"	"	
	3,4-(CH ₂ O) ₂ C ₆ H ₃ (CH ₂) ₂ Br	LDA	
	"	"	
	"	"	
	"	"	
	"	"	
C ₅	<i>i</i> -C ₃ H ₇ CH ₂ CN	C ₂ H ₅ Br	KNH ₂
		<i>i</i> -C ₃ H ₇ Br	Li, (C ₂ H ₅) ₂ NH
		<i>i</i> -C ₃ H ₇ I	NaNH ₂

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

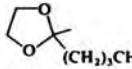
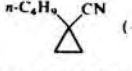


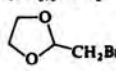
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
HMPA	(CH ₃) ₂ C=CHCH ₂ CH ₂ CH(CH ₃)CN (85)	556
THF, -78°	CH ₂ CH(CH ₂ C ₆ H ₅)CN (62), CH ₂ C(CH ₂ C ₆ H ₅) ₂ CN (12)	537
HMPA	 (86)	168
THF, -78°	C ₆ H ₅ (CH ₂) ₃ CH(CH ₃)CN (65), [C ₆ H ₅ (CH ₂) ₃] ₂ C(CH ₃)CN (32)	537
HMPA, 85°	CH ₂ CH(CH ₂ H ₃)CN (64), CH ₂ C(CH ₂ H ₃) ₂ CN (17)	31
THF, -78°	C ₆ H ₅ (CH ₂) ₄ CH(CH ₃)CN (60), [C ₆ H ₅ (CH ₂) ₄] ₂ C(CH ₃)CN (36)	537
"	C ₆ H ₅ (CH ₂) ₂ CH(CH ₃)CH(CH ₃)CN (60), [C ₆ H ₅ (CH ₂) ₂ CH(CH ₃)] ₂ C(CH ₃)CN (10)	537
NH ₃	(C ₂ H ₅) ₂ CCN (58)	255
NH ₃ , Et ₂ O	" (39)	555
NH ₃	" (49)	255
HMPA, 85°	(C ₂ H ₅) ₂ CCN (55), (C ₂ H ₅) ₂ CHCN (21)	31
"	(C ₂ H ₅) ₂ CCN (75)	31
NH ₃ , Et ₂ O	(CH ₃) ₂ C(CH ₂ H ₃)CN (25)	555
C ₆ H ₆ , HMPA, -60°	C ₂ H ₅ CH[(CH ₂) ₂ Cl]CN (57)	548
HMPA	" (57)	193
NH ₃	C ₂ H ₅ C(C ₂ H ₅ - <i>i</i>) ₂ CN (58)	255
"	" (77)	255
C ₆ H ₆ , HMPA, -60°	(CH ₃) ₂ C[(CH ₂) ₂ Cl]CN (75)	548
Et ₂ O	" (73, crude)	557
C ₆ H ₆ , HMPA, -60°	(CH ₃) ₂ C(C ₂ H ₅ - <i>i</i>)CN (69)	547
THF, -60°	<i>n</i> -C ₄ H ₉ CH(C ₂ H ₅)CN I (54)	552
NH ₃ , Et ₂ O	(<i>n</i> -C ₄ H ₉) ₂ C(C ₂ H ₅)CN II (40)	555
HMPA, -40°	I (48), II (33)	360,361
HMPA, 85°	(C ₂ H ₅) ₂ CHCN I (56), (C ₂ H ₅) ₂ CCN II (22)	31
NH ₃	II (63)	255
HMPA, -70°	(CH ₃) ₂ C(C ₆ H ₅ - <i>n</i>)CN (70)	360,361
C ₆ H ₆ , HMPA, -60°	" (78)	547
"	X(CH ₂) ₄ C(CH ₃) ₂ CN X = Cl I (85)	548
"	X = Br (55)	548
Et ₂ O	I (60)	549
C ₆ H ₆ , HMPA, -60°	ClCH ₂ CH(CH ₃)CH ₂ C(CH ₃) ₂ CN (77)	548
C ₆ H ₆	 (-)	558
C ₆ H ₆ , HMPA, -60°	(<i>sec</i> -C ₅ H ₁₁)C(CH ₃) ₂ CN (81)	547
Et ₂ O	(CH ₃) ₂ C=CHCH ₂ C(CH ₃) ₂ CN (62)	559
"	" (96)	559
C ₆ H ₆ , HMPA, -60°	BrCH ₂ C(CH ₃) ₂ CH ₂ C(CH ₃) ₂ CN (54)	548
THF, -78°	(C ₂ H ₅ O) ₂ CHCH ₂ CH(C ₂ H ₅)CN (-)	165
THF, HMPA, -78°	CH ₂ COCH(CH ₃)CH(C ₂ H ₅)CN (61) ^a	163
C ₆ H ₆ , HMPA	(C ₂ H ₅ O) ₂ CHCH ₂ C(CH ₃) ₂ CN (82)	168
C ₆ H ₆ , toluene	[(CH ₃) ₂ C(CN)CH ₂ Si(CH ₃) ₂] ₂ O (-)	218
Toluene, 80°	(CH ₃) ₂ C(C ₆ H ₁₁)CN (6)	560
HMPA, -60°	(CH ₃) ₂ C(C ₂ H ₅ - <i>n</i>)CN (82)	361
THF, -60°	C ₂ H ₅ CH(C ₆ H ₁₁ - <i>n</i>)CN (55)	553
THF, -78°	" (-)	165
"	C ₂ H ₅ C(C ₆ H ₁₁ - <i>n</i>) ₂ CN (-)	165
"	(CH ₃) ₂ C(C ₆ H ₁₁ - <i>n</i>)CN (80)	555
NH ₃ , Et ₂ O	3,4-(CH ₂ O) ₂ C ₆ H ₃ CH ₂ C(CH ₃) ₂ CN (-)	561
Et ₂ O	(CH ₃) ₂ C[(CH ₂) ₂ OC ₆ H ₅]CN (88)	562
HMPA, 85°	(C ₂ H ₅) ₂ CHCN (75)	31
HMPA, 100°	(CH ₃) ₂ C(C ₂ H ₅)CN (74)	31
"	3,4-(CH ₂ O) ₂ C ₆ H ₃ (CH ₂) ₂ C(CH ₃) ₂ CN	561
"	n = 3 (-)	
"	n = 5 (-)	
NH ₃ , Et ₂ O	<i>i</i> -C ₃ H ₇ C(C ₂ H ₅) ₂ CN (89)	555
C ₆ H ₆ , HMPA, -60°	(<i>i</i> -C ₃ H ₇) ₂ CCN I (22)	547
NH ₃	I (34), (<i>i</i> -C ₃ H ₇) ₂ C=C=NC ₃ H ₇ - <i>i</i> (12) ^a	255

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No of C Atoms	Nucleophile	Electrophile	Base
C ₅ (Contd.)	<i>i</i> -C ₃ H ₇ CH ₂ CN	Cl(CH ₂) ₃ Br	Li, (C ₂ H ₅) ₂ NH
	C ₂ H ₅ CH(CH ₃)CN	<i>n</i> -C ₃ H ₇ Br	NaNH ₂
	<i>i</i> -C ₃ H ₇ CH ₂ CN	Cl(CH ₂) ₄ Br	LiN(C ₂ H ₅) ₂
	C ₂ H ₅ CH(CH ₃)CN	<i>n</i> -C ₄ H ₉ Br	NaNH ₂
		<i>n</i> -C ₃ H ₇ I	NaNH ₂
C ₆	<i>i</i> -C ₃ H ₇ CH ₂ CN	Cl(CH ₂) ₄ Br	LiN(C ₂ H ₅) ₂
	C ₂ H ₅ CH(CH ₃)CN	<i>n</i> -C ₄ H ₉ Br	NaNH ₂
	<i>i</i> -C ₃ H ₇ CH ₂ CN	Cl(CH ₂) ₅ Br	Li, (C ₂ H ₅) ₂ NH
	<i>i</i> -C ₄ H ₉ CH ₂ CN	CH ₃ I	NaNH ₂
	2-Furylacetonitrile	CH ₃ I'	KOH
		"	"
	Pyrazineacetonitrile	CH ₃ I	NaNH ₂
	<i>i</i> -C ₄ H ₉ CH ₂ CN	C ₂ H ₅ Br	"
		CH ₃ OCH ₂ Cl	LDA
	Pyrazineacetonitrile	C ₂ H ₅ Br	NaNH ₂
(C ₂ H ₅) ₂ CHCN	Cl(CH ₂) ₃ Br	LiN(C ₂ H ₅) ₂	
<i>i</i> -C ₄ H ₉ CH ₂ CN	<i>i</i> -C ₃ H ₇ I	NaNH ₂	
	"	LDA	
	CH ₃ O(CH ₂) ₂ Cl	"	
2-Furylacetonitrile	<i>n</i> -C ₃ H ₇ I	"	
	"	KOH	
	"	"	
	"	"	
Pyrazineacetonitrile	<i>n</i> -C ₃ H ₇ Br	NaNH ₂	
	<i>i</i> -C ₃ H ₇ Br	"	
(C ₂ H ₅) ₂ CHCN	Cl(CH ₂) ₄ Br	LiN(C ₂ H ₅) ₂	
(CH ₃) ₂ Si(CH ₂) ₂ CN	(CH ₃) ₂ SiCH ₂ Br	Na	
	(CH ₃) ₂ SiCH ₂ I	"	
<i>i</i> -C ₄ H ₉ CH ₂ CN		Li, (C ₂ H ₅) ₂ NH	
2-Thienylacetonitrile	(CH ₃) ₂ N(CH ₂) ₂ Cl	NaNH ₂	
Pyrazineacetonitrile	<i>n</i> -C ₄ H ₉ Br	"	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

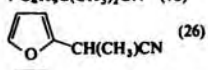
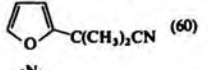
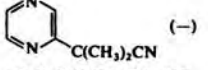
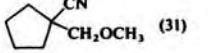
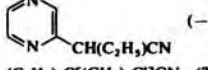
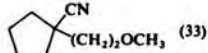
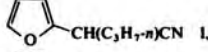
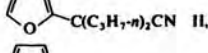
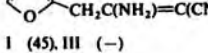
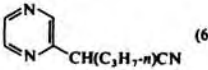
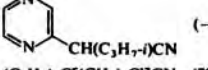
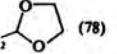
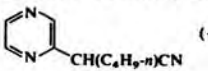




Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ H ₆ , HMPA, -60°	<i>i</i> -C ₃ H ₇ CH[(CH ₂) ₃ Cl]CN (65)	548
"	C ₂ H ₅ C(CH ₃)(C ₃ H ₇ - <i>n</i>)CN (52)	554
HMPA	<i>i</i> -C ₃ H ₇ CH[(CH ₂) ₄ Cl]CN (61)	193
C ₆ H ₆	C ₂ H ₅ C(CH ₃)(C ₄ H ₉ - <i>n</i>)CN (70)	534,554
"	C ₂ H ₅ C(CH ₃)(C ₃ H ₇ - <i>n</i>)CN (68)	554
HMPA	<i>i</i> -C ₃ H ₇ CH[(CH ₂) ₆ Cl]CN (50)	193
"	C ₂ H ₅ C(CH ₃)(C ₄ H ₉ - <i>n</i>)CN (66)	554
C ₆ H ₆ , HMPA	<i>i</i> -C ₃ H ₇ CH(CN)[(CH ₂) ₃ CH(OC ₂ H ₅) ₂]CN (80)	168
NH ₃	<i>i</i> -C ₄ H ₉ C(CH ₃) ₂ CN (78)	255
C ₆ H ₆	 (26)	563
"	 (60)	563
NH ₃ , dioxane	 (-)	272
NH ₃	<i>i</i> -C ₄ H ₉ C(C ₂ H ₅) ₂ CN (65)	255
THF	 (31)	564
NH ₃ , dioxane	 (-)	272
Et ₂ O	(C ₂ H ₅) ₂ C[(CH ₂) ₃ Cl]CN (70)	557
NH ₃	<i>i</i> -C ₄ H ₉ CH(C ₃ H ₇ - <i>i</i>)CN I (43), (<i>i</i> -C ₄ H ₉)(C ₃ H ₇ - <i>i</i>)C=C=NC ₃ H ₇ - <i>i</i> (56) ^f	255
THF, 0°	I (60)	565
THF	 (33)	564
	 I,	
	 II,	
	 III	
C ₆ H ₆	I (45), III (-)	563
Toluene	I (26), III (43)	563
C ₆ H ₆	II (75)	563
NH ₃ , dioxane	 (63)	272
"	 (-)	272
Et ₂ O	(C ₂ H ₅) ₂ C[(CH ₂) ₄ Cl]CN (70)	549
"	[(CH ₃) ₂ SiCH ₂] ₂ CHCN (32)	566
"	" (41)	566
C ₆ H ₆ , HMPA	<i>i</i> -C ₄ H ₉ CH(CN)CH ₂  (78)	168
NH ₃ , toluene	(2-C ₄ H ₉ S)CH[(CH ₂) ₂ N(CH ₃) ₂]CN (42)	567
NH ₃ , dioxane	 (-)	272

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₆ (Contd.)	2-Furylacetonitrile	<i>i</i> -C ₅ H ₁₁ Br ^c	KOH
	2-Thienylacetonitrile	(C ₂ H ₅) ₂ N(CH ₂) ₂ Cl	NaNH ₂
		1-(2-Chloroethyl)pyrrolidine	"
		4-(2-Chloroethyl)morpholine	"
	Pyrazineacetonitrile	(C ₂ H ₅) ₂ N(CH ₂) ₂ Cl	"
	(C ₂ H ₅) ₂ CHCN	C ₆ H ₅ CH ₂ Cl	C ₆ H ₅ Na
		C ₆ H ₅ CH ₂ Cl	LDA
	2-Furylacetonitrile	C ₆ H ₅ CH ₂ Cl ^c	KOH
	"	"	"
	2-Thienylacetonitrile (C ₂ H ₅) ₂ CHCN	1-(2-Chloroethyl)piperidine C ₆ H ₅ O(CH ₂) ₂ Br	NaNH ₂ LiN(C ₂ H ₅) ₂
2-Thienylacetonitrile	(<i>n</i> -C ₃ H ₇) ₂ N(CH ₂) ₂ Cl	NaNH ₂	
		"	
		"	
	(<i>n</i> -C ₄ H ₉) ₂ N(CH ₂) ₂ Cl C ₆ H ₅ CH ₂ N(CH ₃)(CH ₂) ₂ Cl	" "	
C ₇	2-Pyridylacetonitrile	C ₂ H ₅ Br	"
	3-Pyridylacetonitrile	C ₂ H ₅ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	4-Pyridylacetonitrile	C ₂ H ₅ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(CH ₂ CH=CH ₂) ₂]Cl
		<i>i</i> -C ₃ H ₇ Br	Li, (C ₂ H ₅) ₂ NH
		Cl(CH ₂) ₃ Br	LiN(C ₂ H ₅) ₂
	1-Methyl-4-piperidinecarbonitrile	<i>n</i> -C ₃ H ₇ Br	C ₆ H ₅ Na
	2-Pyridylacetonitrile	<i>n</i> -C ₃ H ₇ Cl	NaNH ₂
		<i>i</i> -C ₃ H ₇ Cl	"
		CH ₂ =CHCH ₂ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	NaNH ₂
4-Pyridylacetonitrile	HC≡CCH ₂ Cl	LiNH ₂	
	<i>n</i> -C ₃ H ₇ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

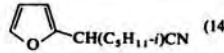


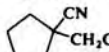
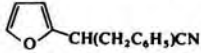
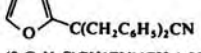


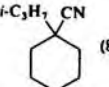
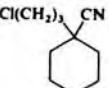
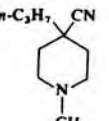

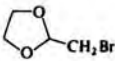

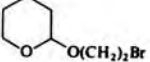

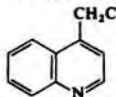
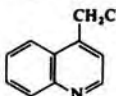
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ H ₆	 (14)	563
NH ₃ , toluene	(2-C ₄ H ₉ S)CH[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN (66)	567
"	(2-C ₄ H ₉ S)CH(CN)(CH ₂) ₂ N(CH ₂) ₄ (58)	567
"	(2-C ₄ H ₉ S)CH(CN)(CH ₂) ₂ N  (43)	567
NH ₃ , dioxane	 (-)	272
C ₆ H ₆	(C ₂ H ₅) ₂ C(CH ₂ C ₆ H ₅)CN (71)	50
THF	 (61)	564
C ₆ H ₆	 (26)	563
"	 (6)	563
NH ₃ , toluene	(2-C ₄ H ₉ S)CH(CN)(CH ₂) ₂ N(CH ₂) ₅ (60)	567
Et ₂ O	(C ₂ H ₅) ₂ C[(CH ₂) ₂ OC ₆ H ₅]CN (75)	562
NH ₃ , toluene	(2-C ₄ H ₉ S)CH[(CH ₂) ₂ N(C ₃ H ₇ - <i>n</i>) ₂]CN (51)	567
"	(2-C ₄ H ₉ S)CH(CN)(CH ₂) ₂ N  (55)	567
NH ₃ , toluene	(2-C ₄ H ₉ S)CH(CN)(CH ₂) ₂ N  (37)	567
NH ₃ , toluene	(2-C ₄ H ₉ S)CH[(CH ₂) ₂ N(C ₄ H ₉ - <i>n</i>) ₂]CN (53)	567
-	(2-C ₄ H ₉ S)CH[(CH ₂) ₂ N(CH ₃ CH ₂ C ₆ H ₅) ₂]CN (41)	568
Toluene	(2-C ₂ H ₅ N)CH(C ₂ H ₅)CN (69)	377
-	" (82)	569
-	(3-C ₂ H ₅ N)CH(C ₂ H ₅)CN (46)	570
-	(4-C ₂ H ₅ N)CH(C ₂ H ₅)CN (69)	569
C ₆ H ₆ , HMPA, -60°	 (85)	547
C ₆ H ₆ , HMPA, -60°	 (67)	548
	 (62)	571
Et ₂ O	(2-C ₃ H ₄ N)C(C ₃ H ₇ - <i>n</i>) ₂ CN (70)	572
"	(2-C ₃ H ₄ N)C(C ₃ H ₇ - <i>i</i>) ₂ CN (47)	572
"	(2-C ₃ H ₄ N)C(CH ₂ CH=CH ₂)CN (79)	569
Et ₂ O	(2-C ₃ H ₄ N)C(CH ₂ CH=CH ₂) ₂ CN (62)	572
NH ₃	(2-C ₃ H ₄ N)C(CH ₂ C≡CH) ₂ CN (44)	573
"	(4-C ₃ H ₄ N)CH(C ₃ H ₇ - <i>n</i>)CN (67)	569

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₇ (Contd.)	4-Pyridylacetonitrile <i>n</i> -C ₆ H ₅ CH(CH ₃)CN (CH ₃) ₂ Si(CH ₂) ₂ CN	CH ₂ =CHCH ₂ Cl C(CH ₂) ₂ Br (CH ₃) ₂ SiCH ₂ I	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl Li, (C ₂ H ₅) ₂ NH Na
			Li, (C ₂ H ₅) ₂ NH
	2-Pyridylacetonitrile	<i>i</i> -C ₄ H ₉ Cl (CH ₃) ₂ N(CH ₂) ₂ Cl	NaNH ₂ "
	4-Pyridylacetonitrile	<i>n</i> -C ₆ H ₅ Br <i>i</i> -C ₄ H ₉ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl "
	2-Pyridylacetonitrile	<i>i</i> -C ₃ H ₇ Cl	NaNH ₂
		(C ₂ H ₅ O) ₂ CHCH ₂ Br	Li, (C ₂ H ₅) ₂ NH
	CH ₂ CH=CH(CH ₂) ₂ CN		LDA
		C ₆ H ₅ CH ₂ Cl	—
		(C ₂ H ₅ O) ₂ CH(CH ₂) ₂ Cl	Li, (C ₂ H ₅) ₂ NH
	2-Pyridylacetonitrile	C ₆ H ₅ CH ₂ Cl	NaNH ₂
		C ₆ H ₅ CH ₂ OH* 4-O ₂ NC ₆ H ₄ CH ₂ Cl C ₆ H ₅ CH ₂ Cl	Na, CH ₃ CO ₂ CH ₂ C ₆ H ₅ NaNH ₂ 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	4-Pyridylacetonitrile	C ₆ H ₅ CH ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	2-Pyridylacetonitrile	<i>n</i> -C ₆ H ₁₁ OH*	Na, CH ₃ CO ₂ C H ₁₇ -n
	3-Pyridylacetonitrile	Ar(CH ₂) ₂ Br	Na, C ₆ H ₅ CO ₂ CH ₃ NaH " " "
	3-Pyridylacetonitrile	4-CH ₂ C ₆ H ₄ (CH ₂) ₂ Br C ₆ H ₅ (CH ₂) ₂ Cl 4-(CH ₂) ₂ NC ₆ H ₄ CH ₂ Cl	" " " "
2-Pyridylacetonitrile	 	NaNH ₂ "	
C ₈	(<i>i</i> -C ₃ H ₇) ₂ CHCN	CH ₃ Br CH ₃ I	NaNH ₂ LDA
	C ₆ H ₅ CH ₂ CN	CH ₃ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

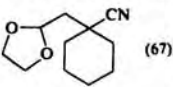




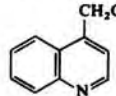
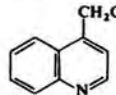




Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ H ₆ , HMPA, -60° Et ₂ O	(4-C ₆ H ₄ N)C(CH ₂ CH=CH ₂) ₂ CN (39) <i>n</i> -C ₆ H ₅ C(CH ₃)[(CH ₂) ₂ Cl]CN (90) (CH ₃) ₂ Si(CH ₂) ₂ CH[CH ₂ Si(CH ₃) ₂]CN (33)	569 548 566
C ₆ H ₆ , HMPA	 (67)	168
Et ₂ O	(2-C ₂ H ₅ N)C(C ₆ H ₅ - <i>i</i>) ₂ CN (68) (2-C ₂ H ₅ N)C[(CH ₂) ₂ N(CH ₃) ₂] ₂ CN (25)	572 572
Et ₂ O	(4-C ₂ H ₅ N)CH(C ₆ H ₅ - <i>n</i>)CN (66) (4-C ₂ H ₅ N)CH(C ₆ H ₅ - <i>i</i>)CN (55) (2-C ₂ H ₅ N)C(C ₂ H ₁₁ - <i>i</i>) ₂ CN (41)	569 569 572
C ₆ H ₆ , HMPA	(C ₂ H ₅ O) ₂ CHCH ₂  (84)	168
THF, HMPA	CH ₂ CH=CH(CH ₂) ₂ CH(CN)(CH ₂) ₂ O  (ca. 50)	222
—	C ₆ H ₅ CH ₂ 	574
C ₆ H ₆ , HMPA	(C ₆ H ₅ O) ₂ CH(CH ₂) ₂  (75)	168
Et ₂ O	(2-C ₂ H ₅ N)CH(CH ₂ C ₆ H ₅)CN (43), (2-C ₂ H ₅ N)C(CH ₂ C ₆ H ₅) ₂ CN I (46) I (60)	575 572 309,311,313
Et ₂ O	(2-C ₂ H ₅ N)CH(CH ₂ C ₆ H ₅)CN (84)* (2-C ₂ H ₅ N)C(CH ₂ C ₆ H ₄ NO ₂ -4) ₂ CN (45)	572 569
—	(4-C ₂ H ₅ N)CH(CH ₂ C ₆ H ₅)CN (2-C ₂ H ₅ N)CH(C ₆ H ₁₁ - <i>n</i>)CN (84)* " (84)*	314 312
DMF, toluene	(3-C ₂ H ₅ N)CH[(CH ₂) ₂ Ar]CN I I, Ar = C ₆ H ₅ (-) I, Ar = 3-ClC ₆ H ₄ (-) I, Ar = 4-ClC ₆ H ₄ (-)	576 576 576
DMF, toluene	(3-C ₂ H ₅ N)CH[(CH ₂) ₂ C ₆ H ₄ CH ₂ -4]CN (-) (3-C ₂ H ₅ N)CH[(CH ₂) ₂ C ₆ H ₅]CN (-)	576 576
DMF	(3-C ₂ H ₅ N)CH[CH ₂ C ₆ H ₄ N(CH ₂) ₂ -4]CN (-)	342
C ₆ H ₆	CH ₂ CH(C ₂ H ₅ N-2)CN  (-)	826
—	CH ₂ CH(C ₂ H ₅ N-2)CN  (83)	826
NH ₃ THF, 0°	(<i>i</i> -C ₃ H ₇) ₂ C(CH ₃)CN (81) " (100)	255 565
—	C ₆ H ₅ CH(CH ₃)CN I, C ₆ H ₅ C(CH ₃) ₂ CN II II (-)	66

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₆ (Contd.)	C ₆ H ₅ CH ₂ CN	CH ₃ Br	"
	"	CH ₃ I	NaOH
	"	CH ₃ I	LiH
	"	"	50% aq NaOH, (C ₂ H ₅ O) ₂ POCH ₂ SC ₆ H ₅
	"	"	<i>t</i> -C ₄ H ₉ OK
	"	"	(<i>n</i> -C ₄ H ₉) ₄ NOH
	"	"	NaNH ₂
	"	"	"
	"	"	"
	"	"	"
	"	"	KNH ₂
	"	"	LICA
	"	"	C ₁₀ H ₈ Na
	"	"	CH ₃ Li
	"	"	K ₂ C ₈
	"	CH ₂ Cl ₂	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl or [CH ₂ =CHCH ₂ N(C ₂ H ₅) ₃]Cl
	"	CH ₃ I ^c	NaNH ₂
	"	"	"
	"	"	<i>t</i> -C ₃ H ₇ ONa
	"	"	NaH
	"	"	"
	"	"	"
	2-ClC ₆ H ₄ CH ₂ CN	"	"
3-ClC ₆ H ₄ CH ₂ CN	"	"	
4-ClC ₆ H ₄ CH ₂ CN	"	"	
2,4-Cl ₂ C ₆ H ₃ CH ₂ CN	"	"	
2,5-Cl ₂ C ₆ H ₃ CH ₂ CN	"	"	
2,6-Cl ₂ C ₆ H ₃ CH ₂ CN	"	"	
3,4-Cl ₂ C ₆ H ₃ CH ₂ CN	"	"	
2,3,6-Cl ₃ C ₆ H ₂ CH ₂ CN	"	"	
4-O ₂ NC ₆ H ₄ CH ₂ CN	ClCN	"	
	CH ₃ Cl	NaNH ₂	
	CH ₃ I	"	
	CH ₃ Cl	"	
	"	"	
(<i>i</i> -C ₃ H ₇) ₂ CHCN	C ₂ H ₅ Br	"	
C ₆ H ₅ CH ₂ CN	(CH ₃) ₂ SO ₄	"	
"	"	KOH	
"	"	NaNH ₂	
"	"	"	
"	"	LDA	
(<i>i</i> -C ₃ H ₇) ₂ CHCN	C ₂ H ₅ I	"	
C ₆ H ₅ CH ₂ CN	C ₂ H ₅ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	
"	"	NaNH ₂	
"	C ₂ H ₅ Br	LiH	
"	"	NaOH	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

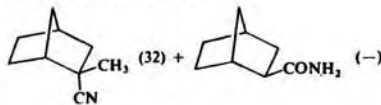
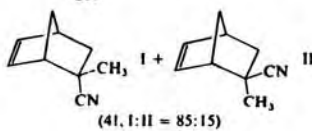
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
-	I (55)	65,577
Aq DMSO	I (79), II (8)	96
C ₆ H ₆	I (46)	578
-	I (66), II (28)	579
<i>t</i> -C ₄ H ₉ OH	I (52)	580
Aq CH ₂ Cl ₂ or CHCl ₃	I (72), ^f II (14) ^f	80
Et ₂ O	I (54), II (11)	161
NH ₃ , Et ₂ O	I (58), II (14)	162
Toluene	I (62), II (16)	162
NH ₃ , Et ₂ O	I (89)	581
C ₆ H ₆	I (87)	580
NH ₃ , Et ₂ O	I (50), II (19)	161
THF, -78°	I (70), II (30)	537
THF	I (46)	198
Et ₂ O, THF, -100°	II (95)	44
THF, -60°	I (60), II (6)	552
-	[C ₆ H ₅ CH(CN)] ₂ CH ₂ (80)	70,582
C ₆ H ₆	2-ClC ₆ H ₄ C(CH ₃) ₂ CN (12)	583
"	3-ClC ₆ H ₄ C(CH ₃) ₂ CN (23)	583
"	4-ClC ₆ H ₄ C(CH ₃) ₂ CN (89)	584
Toluene	4-ClC ₆ H ₄ CH(CH ₃)CN (51)	585
"	2,4-Cl ₂ C ₆ H ₃ CH(CH ₃)CN (-)	585
"	2,5-Cl ₂ C ₆ H ₃ CH(CH ₃)CN (-)	585
"	2,6-Cl ₂ C ₆ H ₃ CH(CH ₃)CN (51)	585
"	3,4-Cl ₂ C ₆ H ₃ CH(CH ₃)CN (63)	585
"	2,3,6-Cl ₃ C ₆ H ₂ CH(CH ₃)CN (58)	585
THF	4-O ₂ NC ₆ H ₄ CH(CH ₃)CN (79)	586,587
Toluene		588
C ₆ H ₆		177
NH ₃	I (37)	588
"	I (77)	588
NH ₃	(<i>i</i> -C ₃ H ₇) ₂ C(C ₂ H ₅)CN (78)	255
DMF	C ₆ H ₅ CH(CH ₃)CN I, C ₆ H ₅ C(CH ₃) ₂ CN II	
NH ₃ , Et ₂ O	I (-)	203
C ₆ H ₆	I (80)	589
THF, 0°	I (82)	290
"	(<i>i</i> -C ₃ H ₇) ₂ C(C ₂ H ₅)CN (97)	565
"	C ₆ H ₅ CH(C ₂ H ₅)CN I, C ₆ H ₅ C(C ₂ H ₅) ₂ CN II	
"	I (88)	65,68
Et ₂ O	II (-)	590
C ₆ H ₆	I (30)	578
NH ₃	I (76)	289,591

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₆ (Contd.)	C ₆ H ₅ CH ₂ CN	C ₂ H ₅ Br	50% aq NaOH, CH ₃ BF ₄ ⁻ 
		"	"
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	50% aq NaOH, (n-C ₄ H ₉) ₃ N
		"	50% aq NaOH, dibenzo[18]crown-6
		"	NaOH, KOH
		"	(n-C ₄ H ₉) ₄ NOH
		"	NaNH ₂
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
C ₆ H ₅ CH ₂ ¹⁴ CN C ₆ H ₅ CD ₂ CN C ₆ H ₅ CH ₂ CN	C ₂ H ₅ I	NaH	Aq NaOH, (n-C ₄ H ₉) ₄ NI
		"	i-C ₄ H ₉ OK
		"	NaNH ₂
		"	"
		"	Mg
		"	n-C ₄ H ₉ MgBr
		"	C ₁₀ H ₈ Mg
		"	Na, CH ₃ CO ₂ C ₂ H ₅
		"	Na, C ₆ H ₅ CO ₂ CH ₃
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	"
		"	NaNH ₂
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	NaNH ₂
		"	"
4-ClC ₆ H ₄ CH ₂ CN	C ₂ H ₅ Br	"	"
		"	"
		"	"
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		"	"
		4-BrC ₆ H ₄ CH ₂ CN 4-H ₂ NC ₆ H ₄ CH ₂ CN	C ₂ H ₅ Br
"	"		
"	"		
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"	"		
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"	"		
"	"		
"	"		
"	"		
"	"		
4-XC ₆ H ₄ CH ₂ CN	C ₂ H ₅ Br		
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
			C ₂ H ₅ Br
"	"		
"	"		
"	"		
"	"		
"	"		
"	"		
"	"		
"	"		
"	"		
"	"		
"	"		
"	"		
"	"		
(i-C ₃ H ₇) ₂ CHCN	C ₂ H ₅ I		
		KNH ₂	"
		LiNH ₂	"
		LDA	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		C ₆ H ₅ CH ₂ CN	n-C ₃ H ₇ Cl
"	"		
"	"		
"	"		
"	"		
"	"		
"	"		
"	"		
"	"		
"	"		
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ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

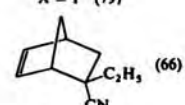
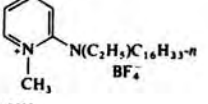
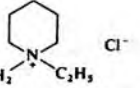
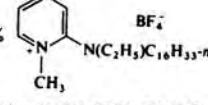
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	I (90), II (3)	592
	I (90)	68,85,98,577
	II (100)	593
	I (85)	527
	I (94)	594
	I (100) ^f	80
Aq CH ₂ Cl ₂ or CHCl ₃	I (82)	290,595
C ₆ H ₆	II (-)	583
Toluene	I (92)	596
NH ₃	I (69-70)	597
Et ₂ O	C ₆ H ₅ CH(C ₂ H ₅) ¹⁴ CN (89)	598
DMF, C ₆ H ₆	C ₆ H ₅ CD(C ₂ H ₅)CN (80)	385
	I (90)	227
i-C ₄ H ₉ OH	I (64)	580
Et ₂ O	I (62-84)	599
C ₆ H ₆	I (80-85)	580
NH ₃ , Et ₂ O	I (42)	600
HMPA, 80°	I (80), II (2)	31
Et ₂ O	I (35)	601
-	I (63) ^f	314
-	I (63) ^f	312
-	C ₆ H ₅ CH(CN)CH ₂ CH(CN)C ₆ H ₅ (-)	72
-	C ₆ H ₅ C(CH ₂ OCH ₃)(CN)CH ₂ CH(CN)C ₆ H ₅ (68)	72
NH ₃ , Et ₂ O	C ₆ H ₅ CH(CH ₂ CN)CN I (41), C ₆ H ₅ C(CH ₂ CN) ₂ CN II (ca. 9)	602
	I (ca. 70)	75
	II (15)	603
C ₆ H ₆	C ₆ H ₅ CH(CH ₂ CO ₂ H)CN (-)	546
NH ₃	4-ClC ₆ H ₄ C(C ₂ H ₅) ₂ CN (32)	583
C ₆ H ₆	" (79)	604
Et ₂ O	4-BrC ₆ H ₄ CH(C ₂ H ₅)CN (-)	595
C ₆ H ₆	4-H ₂ NC ₆ H ₄ C(C ₂ H ₅) ₂ CN (40), 4-H ₂ NC ₆ H ₄ CH(C ₂ H ₅)CN (9), 4-[(C ₂ H ₅) ₂ N]C ₆ H ₄ C(C ₂ H ₅) ₂ CN (12)	605
Et ₂ O	4-XC ₆ H ₄ C(CH ₂ CN) ₂ CN I	75
	I X = H (41)	
	X = F (36)	
	X = Cl (83)	
	X = Br (81)	
	X = I (79)	
NH ₃ , toluene	 (66)	588
	" (85)	178
THF, -78°	(i-C ₃ H ₇) ₂ CCN I (33), (i-C ₃ H ₇) ₂ C=C=NC ₃ H ₇ -i II (25) ^f	255
NH ₃	I (39), II (26) ^f	255
"	I (70), II (23)	565
THF, 0°	I (37-50), II (23-25) ^f	255
NH ₃	I (42-45), II (19-26) ^f	255
"	C ₆ H ₅ CH(C ₃ H ₇ -n)CN I, C ₆ H ₅ C(C ₃ H ₇ -n) ₂ CN II	606,98
-	I (66)	578
C ₆ H ₆	I (45)	96
Aq DMSO	I (75), II (13)	65,68
-	I (78)	290,595,607
C ₆ H ₆	I (88)	583
"	II (41)	

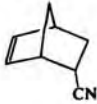
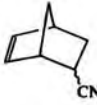
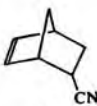

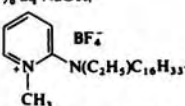
TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base	
C ₈ (Contd.)	C ₆ H ₅ CH ₂ CN	<i>n</i> -C ₃ H ₇ Br	NaNH ₂	
		"	"	
		"	Mg	
		"	C ₁₀ H ₈ Na	
		<i>n</i> -C ₃ H ₇ I	<i>i</i> -C ₄ H ₉ OK	
		"	NaNH ₂	
		<i>n</i> -C ₃ H ₇ OH*	Na, CH ₃ CO ₂ C ₃ H ₇ - <i>n</i>	
		"	Na, C ₆ H ₅ CO ₂ CH ₃	
		<i>i</i> -C ₃ H ₇ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
		<i>i</i> -C ₃ H ₇ Br	"	
		"	50% aq NaOH.	
		"		
		"	NaNH ₂	
		"	"	
		"	LICA	
		"	K ₂ C ₈	
		<i>i</i> -C ₃ H ₇ I	(<i>n</i> -C ₄ H ₉) ₂ NOH	
		"	NaNH ₂	
		"	Mg	
		<i>i</i> -C ₃ H ₇ OH*	Na, CH ₃ CO ₂ C ₃ H ₇ - <i>i</i>	
		"	Na, C ₆ H ₅ CO ₂ CH ₃	
		CH ₂ =CHCH ₂ Cl		
				
				KOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		CH ₂ =CHCH ₂ Cl	NaH	
"	NaNH ₂			
CH ₂ =CHCH ₂ Br	50% aq NaOH.			
		3% 		
CH ₂ =CHCH ₂ Br or CH ₂ =CHCH ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl			
"	LICA			
"	Mg			
HC≡CCH ₂ Cl	LiNH ₂			
HC≡CCH ₂ Br	NaNH ₂			
Cl(CH ₂) ₃ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl			
"	Li(C ₂ H ₅) ₂			
Cl(CH ₂) ₃ Br	Aq NaOH, (<i>n</i> -C ₄ H ₉) ₂ NI			
"	NaNH ₂			
Cl(CH ₂) ₃ I	50% aq NaOH.			
		[(C ₆ H ₅ CH ₂) ₂ N(C ₂ H ₅) ₂] ₂ SO ₄		
Br(CH ₂) ₃ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl			
"	Aq NaOH, (<i>n</i> -C ₄ H ₉) ₂ NI			
CH ₃ OCH(CH ₃)Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl			
ClCH ₂ CO ₂ CH ₃	NaNH ₂			
BrCH(CH ₃)CO ₂ Na	"			
Br(CH ₂) ₂ CN	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl			
<i>i</i> -C ₃ H ₇ Br	"			
<i>i</i> -C ₃ H ₇ Cl	50% aq NaOH, [(<i>n</i> -C ₄ H ₉) ₂ N]Cl			

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NH ₃	I (64)	597
NH ₃ , Et ₂ O	I (69), II (14)	162
NH ₃	I (57)	608
THF	I (-)	198
<i>i</i> -C ₄ H ₉ OH	I (45)	580
-	I (70)	609
-	I (72) ^f	314
-	I (61) ^f	312
-	C ₆ H ₅ CH(C ₃ H ₇ - <i>i</i>)CN I, C ₆ H ₅ C(C ₃ H ₇ - <i>i</i>) ₂ CN II	
-	I (2)	68
-	I (ca. 80)	610,65,68
-	I (23)	592
Toluene or C ₆ H ₆	I (76), II (2)	162,539,607,611
NH ₃ , Et ₂ O	I (90), II (7)	162
THF, -78°	I (75), II (16)	537
THF, -60°	I (58), II (6)	552
Aq CH ₂ Cl ₂ or CHCl ₃	I (75) ^f	80
Et ₂ O	I (-), II (-)	612
NH ₃	I (69)	608
-	I (57) ^f	314
-	I (57) ^f	312
	C ₆ H ₅ CH(CH ₂ CH=CH ₂)CN I, C ₆ H ₅ C(CH ₂ CH=CH ₂) ₂ CN II	
Aq C ₂ H ₅ OH	I (90)	570
-	I (89)	606
DMSO	II (92)	204
C ₆ H ₆	I (-)	595
-	I (63), II (34)	592
-	I (60)	577
THF, -78°	I (70), II (26)	537
NH ₃	I (50)	608
NH ₃	C ₆ H ₅ C(CH ₂ C≡CH) ₂ CN I (44)	573
Et ₂ O, C ₆ H ₆	C ₆ H ₅ CH(CH ₂ C≡CH)CN (30), I (70)	613
-	C ₆ H ₅ CH[(CH ₂) ₃ Cl]CN (47)	70
-	" (81)	557
-	" (95)	227
C ₆ H ₆ or toluene	" (-)	595,614
-	" (-)	615
-	C ₆ H ₅ CH[(CH ₂) ₃ Br]CN (20)	70
-	[C ₆ H ₅ CH(CN)CH ₂] ₂ CH ₂ (96)	227
-	[C ₆ H ₅ CH(CN)] ₂ CHCH ₃ (70)	72
C ₆ H ₆	C ₆ H ₅ C(CH ₂ CO ₂ CH ₃) ₂ CN (12)	603
NH ₃	C ₆ H ₅ CH[CH(CH ₃)CO ₂ H]CN (-)	546
-	C ₆ H ₅ C(CH ₂ CH ₂ CN) ₂ CN (-)	73
-	4-ClC ₆ H ₄ CH(C ₃ H ₇ - <i>i</i>)CN (91)	610,616
-	" (89-93)	617

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₈ (Cont'd.)	4-ClC ₆ H ₄ CH ₂ CN	<i>i</i> -C ₃ H ₇ Cl	KOH
	XC ₆ H ₄ CH ₂ CN	Br(CH ₂) ₂ Cl	NaNH ₂
			"
			"
			"
	4-H ₂ NC ₆ H ₄ CH ₂ CN	<i>n</i> -C ₃ H ₇ Br	"
		<i>i</i> -C ₃ H ₇ Br	"
		CH ₂ =CHCH ₂ Br	"
		"	"
		<i>n</i> -C ₃ H ₇ Br'	"
		<i>i</i> -C ₃ H ₇ Br'	"
		CH ₂ =CHCH ₂ Br	"
		"	"
		"	"
		CH ₂ =CHCH ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	(<i>i</i> -C ₃ H ₇) ₂ CHCN	<i>i</i> -C ₄ H ₉ Br	KNH ₂
		(CH ₂) ₂ N(CH ₂) ₂ Cl	NaNH ₂
	C ₆ H ₅ CH ₂ CN	<i>n</i> -C ₄ H ₉ Cl	NaOH
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	NaH
		<i>n</i> -C ₄ H ₉ Br	LiH
		"	KOH
		"	50% aq NaOH, Dowex-1-X8 (triphase)
		"	50% aq NaOH, (<i>n</i> -C ₄ H ₉) ₄ NBr
		"	K ₂ C ₈
		"	50% aq NaOH,
			
		"	50% aq KOH, (<i>n</i> -C ₄ H ₉) ₂ N or (<i>n</i> -C ₄ H ₉) ₄ NI
		"	50% aq NaOH, [C ₆ H ₅ N(CH ₂) ₂]Br or [C ₆ H ₅ CH ₂ N(CH ₂) ₂]Br
		"	50% aq NaOH (no catalyst)
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	NaNH ₂
		"	"
		"	"
		"	<i>n</i> -C ₄ H ₉ Li

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

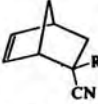
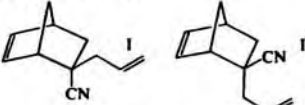

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	" (98)	617,618
—	XC ₆ H ₄ CH[(CH ₂) ₂ Cl]CN	
—	X = 4-Cl (—)	614
—	X = 3-Cl (—)	614
—	X = 2-Cl (—)	614
—	X = 4-F (—)	614
Et ₂ O	4-H ₂ NC ₆ H ₄ CH(C ₃ H _{7-<i>n</i>})CN (2), 4-H₂NC₆H₄C(C₃H_{7-<i>n</i>})₂CN (70), 4-(<i>n</i>-C₃H₇NH)C₆H₄C(C₃H_{7-<i>n</i>})₂CN (3)}}}	605
"	4-H ₂ NC ₆ H ₄ CH(C ₃ H _{7-<i>i</i>})CN (3), 4-H₂NC₆H₄C(C₃H_{7-<i>i</i>})₂CN (30), 4-(<i>i</i>-C₃H₇NH)C₆H₄C(C₃H_{7-<i>i</i>})₂CN (20)}}}	605
"	4-H ₂ NC ₆ H ₄ C(CH ₂ CH=CH ₂) ₂ CN I (61)	619
"	I (62), 4-H ₂ NC ₆ H ₄ CH(CH ₂ CH=CH ₂)CN (5), 4-((CH ₂ =CHCH ₂) ₂)N ₂ C ₆ H ₄ C(CH ₂ CH=CH ₂) ₂ CN (8)	605
NH ₃ , toluene	 I, R = C ₃ H _{7-<i>n</i>"} (79)}	620
"	I, R = C ₃ H _{7-<i>i</i>"} (63)}	620
C ₆ H ₆	 I, II (17, I:II = 86:14)	177
NH ₃ , toluene	I (42)	620
—	 (86)	569
NH ₃ , —	(<i>i</i> -C ₃ H ₇) ₂ C(C ₆ H _{5-<i>i</i>})CN (84)}	255
NH ₃ , Et ₂ O	(<i>i</i> -C ₃ H ₇) ₂ C[(CH ₂) ₂ N(CH ₂) ₂]CN (—)	621
Aq DMSO	C ₆ H ₅ CH(C ₆ H _{5-<i>n</i>})CN I, C₆H₅C(C₆H_{5-<i>n</i>})₂CN II}}	
—	I (62), II (8)	96
—	I (17)	68
DME	I (73), II (9)	162
C ₆ H ₆	I (4)	578
DMF	I (—)	203
—	I (85-84), II (3-7)	99,622
—	I (35-86), II (1-11)	99,622
THF, -60°	I (67), II (3)	552
—	I (65), II (6)	592
110°	I (87-97)	623
—	I (—), II (—)	528
—	I (ca. 70)	92
—	I (74)	65,68
Toluene	I (82), II (5)	162
NH ₃	I (63-69)	597,624
NH ₃ , Et ₂ O	I (60-77), II (5-13)	162
THF, 25°	I (17), II (68-69)	47,46

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₈ (Contd.)	C ₆ H ₅ CH ₂ CN	<i>n</i> -C ₄ H ₉ Br	<i>n</i> -C ₄ H ₉ Li
		<i>n</i> -C ₄ H ₉ OH ⁺	Na, CH ₃ CO ₂ C ₄ H ₉ - <i>n</i>
		<i>n</i> -C ₄ H ₉ I	NaH
		"	<i>i</i> -C ₄ H ₉ OK
		"	NaNH ₂
		<i>sec</i> -C ₄ H ₉ Br	"
		"	"
		"	Na ₂ O
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		<i>sec</i> -C ₄ H ₉ OH ⁺	Na, CH ₃ CO ₂ C ₄ H ₉ - <i>sec</i>
		<i>i</i> -C ₄ H ₉ Br	NaH
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	NaNH ₂
		<i>i</i> -C ₄ H ₉ OH ⁺	Na, CH ₃ CO ₂ C ₄ H ₉ - <i>i</i>
		CH ₃ CHBr(CH ₂) ₂ Br	Aq NaOH, cat (<i>n</i> -C ₄ H ₉) ₄ Nl
		(C ₂ H ₅) ₂ SO ₄	<i>n</i> -C ₄ H ₉ MgBr
		C(CH ₃) ₂ CN	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		CICH ₂ CH(CH ₃)CN	NaNH ₂
		(CH ₃) ₂ N(CH ₂) ₂ Cl	"
		CH ₃ CO ₂ (CH ₂) ₂ Cl	"
CICH ₂ CO ₂ C ₂ H ₅	Mg		
BrCH ₂ CO ₂ C ₂ H ₅	K ₂ CO ₃ , 18-crown-6		
CICH ₂ CO ₂ C ₂ H ₅	NaNH ₂		
<i>n</i> -C ₄ H ₉ Br	"		
<i>i</i> -C ₄ H ₉ Br	"		
		<i>n</i> -C ₄ H ₉ Br	"
		"	"
(i-C ₃ H ₇) ₂ CHCN C ₆ H ₅ CH ₂ CN	<i>n</i> -C ₄ H ₉ I ⁺	LICA	
	(CH ₃) ₂ N(CH ₂) ₂ Cl	NaNH ₂	
	"	"	
	<i>n</i> -C ₃ H ₇ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
	<i>n</i> -C ₃ H ₇ Br	NaNH ₂	
	"	"	
	<i>n</i> -C ₃ H ₇ OH ⁺	Na, CH ₃ CO ₂ C ₃ H ₇ - <i>n</i>	
	<i>i</i> -C ₃ H ₇ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
	"	NaNH ₂	
	"	"	
<i>i</i> -C ₃ H ₇ OH ⁺	Na, CH ₃ CO ₂ C ₃ H ₇ - <i>i</i>		
CH ₃ CHBrC ₂ H ₄ - <i>i</i>	NaNH ₂		
CH ₃ CH=CHCH(CH ₃)Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl		
	KOH		

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

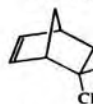
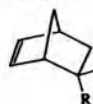
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
THF	I (73)	46	
—	I (75) ⁺	314	
HMPA	I (86), II (—)	625	
<i>i</i> -C ₄ H ₉ OH	I (39)	580	
C ₆ H ₆	I (70)	580,290,607	
NH ₃ , Et ₂ O	C ₆ H ₅ CH(C ₄ H ₉ - <i>sec</i>)CN I, C ₆ H ₅ C(C ₄ H ₉ - <i>sec</i>) ₂ CN II	162	
C ₆ H ₆	I (93), II (1)	290,607,626, 627	
—	I (86)	162	
Toluene	I (58), II (some?)	734	
—	I (—)	65,68	
—	I (63)	314	
—	I (38) ⁺	314	
Toluene	C ₆ H ₅ CH(C ₄ H ₉ - <i>i</i>)CN I, C ₆ H ₅ C(C ₄ H ₉ - <i>i</i>) ₂ CN II	539	
—	I (66)	65,68	
—	I (47)	162	
NH ₃ , Et ₂ O	I (46), II (23)	314	
—	I (68) ⁺	227	
—	C ₆ H ₅ CH[(CH ₂) ₂ CHBrCH ₃]CN (91)	31	
HMPA, 80°	C ₆ H ₅ CH(C ₂ H ₅)CN (51), C ₆ H ₅ C(C ₂ H ₅) ₂ CN (14)	73	
—	C ₆ H ₅ CH[(CH ₂) ₂ CN]CN (—)	73	
—	C ₆ H ₅ C[CH ₂ CH(CH ₃)CN] ₂ CN (16)	628	
Et ₂ O	C ₆ H ₅ CH[(CH ₂) ₂ N(CH ₃) ₂]CN (—)	341	
Dioxane	C ₆ H ₅ CH[(CH ₂) ₂ OCOCH ₃]CN (80)	603	
C ₆ H ₆	C ₆ H ₅ C(CH ₂ CO ₂ C ₂ H ₅) ₂ CN (35)	608	
NH ₃	C ₆ H ₅ CH(CH ₂ CO ₂ C ₂ H ₅)CN (34)	304	
120°	" (45)	605	
Et ₂ O	4-H ₂ NC ₆ H ₄ C(C ₄ H ₉ - <i>n</i>) ₂ CN (40), 4-H ₂ NC ₆ H ₄ CH(C ₄ H ₉ - <i>n</i>)CN (15), 4-(<i>n</i> -C ₄ H ₉) ₂ N(C ₄ H ₉ - <i>n</i>) ₂ CN (5)	605	
—	4-H ₂ NC ₆ H ₄ C(C ₄ H ₉ - <i>i</i>) ₂ CN (37), 4-(<i>i</i> -C ₄ H ₉) ₂ NC ₆ H ₄ C(C ₄ H ₉ - <i>i</i>) ₂ CN (4)	605	
		I, R = <i>n</i> -C ₄ H ₉ (67)	620
		"	"
NH ₃ , toluene	I + II, R = C ₄ H ₉ - <i>n</i> (75, 87:13 = 1:II)	177	
C ₆ H ₆	"	"	
THF, -78°	I + II, R = C ₄ H ₉ - <i>n</i> (90)	178	
NH ₃ , toluene	I, R = (CH ₂) ₂ N(CH ₃) ₂ (40)	620	
—	(<i>i</i> -C ₃ H ₇) ₂ C[(CH ₂) ₂ N(CH ₃) ₂]CN (—)	629	
—	C ₆ H ₅ CH(C ₃ H ₇ - <i>n</i>)CN I, C ₆ H ₅ C(C ₃ H ₇ - <i>n</i>) ₂ CN II	68	
—	I (13)	65,68	
NH ₃ , Et ₂ O	I (72)	162	
C ₆ H ₆	I (81), II (8)	607	
—	I (—)	314	
—	I (67) ⁺	65,68	
—	C ₆ H ₅ CH(C ₃ H ₇ - <i>i</i>)CN I, C ₆ H ₅ C(C ₃ H ₇ - <i>i</i>) ₂ CN II	597	
—	I (56)	162	
NH ₃	I (56-58)	162	
NH ₃ , Et ₂ O	I (70), II (8)	314	
—	I (72) ⁺	627	
C ₆ H ₆	C ₆ H ₅ CH[CH(CH ₃)C ₃ H ₇ - <i>i</i>]CN (—)	627	
—	C ₆ H ₅ CH[CH(CH ₃)CH=CHCH ₃]CN (96)	65,68	
DMF	CH(C ₆ H ₅)CN (—)	203	



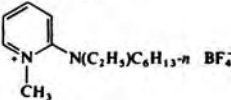
TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₈ (Contd.)	C ₆ H ₅ CH ₂ CN		NaNH ₂
			"
		CH(CH ₃) ₂ Cl (CH ₃) ₂ N(CH ₂) ₂ Cl (CH ₃) ₂ NCH ₂ CH(CH ₃)Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂
		Br(CH ₂) ₂ C(CH ₂) ₂ NO ₂ CH ₃ CHBrCO ₂ C ₂ H ₅ BrCH ₂ CO ₂ C ₂ H ₅ - <i>l</i>	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl Mg 40% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	4-ClC ₆ H ₄ CH ₂ CN	2-(Chloromethyl)furan	NaH
		"	NaNH ₂
	"	<i>n</i> -C ₅ H ₁₁ Br ^{<i>f</i>}	"
	"	<i>i</i> -C ₅ H ₁₁ Br ^{<i>f</i>}	"
	<i>n</i> -C ₄ H ₉ CH(C ₂ H ₅)CN C ₆ H ₅ CH ₂ CN	(C ₂ H ₅ O) ₂ CHCH ₂ Br <i>n</i> -C ₆ H ₁₃ Br " " <i>n</i> -C ₆ H ₁₃ OH ^{<i>f</i>} " Br(CH ₂) ₆ Br " (C ₂ H ₅) ₂ N(CH ₂) ₂ Cl " " " " 4-(2-Chloroethyl)morpholine " " Br(CH ₂) ₂ CN (C ₂ H ₅ O) ₂ CHCH ₂ Br BrCH ₂ CO ₂ C ₄ H ₉ - <i>f</i> C ₆ H ₁₁ Cl C ₆ H ₁₁ Br " " C ₆ H ₁₁ I C ₆ H ₁₁ OH ^{<i>f</i>} "	Li, (C ₂ H ₅) ₂ NH Aq NaOH, (<i>n</i> -C ₄ H ₉) ₄ NI 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂ Na, CH ₃ CO ₂ C ₄ H ₉ - <i>n</i> Na, C ₆ H ₅ CO ₂ CH ₃ Aq NaOH, (<i>n</i> -C ₄ H ₉) ₄ NI " 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl KOH C ₁₀ H ₈ Na NaOH " " " NaNH ₂ " " Na C ₁₀ H ₈ Na Na, CH ₃ CO ₂ C ₄ H ₉ Na, C ₆ H ₅ CO ₂ CH ₃

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₂ O	" (85-90)	630
Xylene	" (41)	631
Toluene	 (55)	339
—	C ₆ H ₅ CH[(CH ₂) ₂ Cl]CN (—)	70
C ₆ H ₆	C ₆ H ₅ CH[(CH ₂) ₂ N(CH ₃) ₂]CN (62)	632
Toluene	C ₆ H ₅ CH[CH(CH ₃)CH ₂ N(CH ₃) ₂]CN (—), C ₆ H ₅ CH[CH ₂ CH(CH ₃)N(CH ₃) ₂]CN (—)	633
—	C ₆ H ₅ CH[(CH ₂) ₂ C(CH ₃) ₂ NO ₂]CN (21)	74
NH ₃	C ₆ H ₅ CH[CH(CH ₃)CO ₂ C ₂ H ₅]CN (63)	608
—	C ₆ H ₅ CH[CH ₂ CO ₂ C ₂ H ₅ - <i>f</i>]CN (—), C ₆ H ₅ C[CH ₂ CO ₂ C ₂ H ₅ - <i>f</i>]CN (—)	77
C ₆ H ₆	(2-C ₄ H ₉ O)CH ₂ CH(C ₆ H ₅)CN	634
"	(2-C ₄ H ₉ O)CH ₂ CH(C ₆ H ₄ Cl-4)CN (96)	634
—	" (—)	635
NH ₃ , toluene	 C ₅ H _{11-n} (66)	620
—	 C ₅ H _{11-i} (65)	620
C ₆ H ₆ , HMPA	<i>n</i> -C ₄ H ₉ C(C ₂ H ₅)[CH ₂ CH(OC ₂ H ₅) ₂]CN (73)	168
—	C ₆ H ₅ CH(C ₆ H _{13-n})CN (94)	227
—	" (85)	65,68
Toluene or C ₆ H ₆	" (79)	290,611,607
—	" (70) ^{<i>f</i>}	314
—	" (70) ^{<i>f</i>}	312
—	C ₆ H ₅ CH[(CH ₂) ₄ Br]CN (85)	227
—	[C ₆ H ₅ CH(CN)(CH ₂) ₂] ₂ (87)	227
—	C ₆ H ₅ CH[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN (—)	65
DMF	" (—)	203
THF	" (64)	198
HO(CH ₂) ₂ OH	" (—)	69
Et ₂ O	" (—)	628
C ₆ H ₆	C ₆ H ₅ CH(CN)(CH ₂) ₂ N (80)	632
Et ₂ O	" (—)	628
—	C ₆ H ₅ CH[(CH ₂) ₂ CN]CN (—)	636
Et ₂ O	C ₆ H ₅ CH[CH ₂ CH(OC ₂ H ₅) ₂]CN (—)	637,638
—	C ₆ H ₅ CH[CH ₂ CO ₂ C ₄ H ₉ - <i>f</i>]CN (—), C ₆ H ₅ C[CH ₂ CO ₂ C ₄ H ₉ - <i>f</i>]CN (—)	77
DMF	C ₆ H ₅ C(C ₆ H ₁₁) ₂ CN (—)	203
NH ₃ , Et ₂ O	C ₆ H ₅ CH(C ₆ H ₁₁)CN I (37), C ₆ H ₅ C(C ₆ H ₁₁) ₂ CN II (4)	162
Toluene	I (65-77), II (some?)	162,639
Xylene	I (62)	631
Toluene	I (54)	640
THF	I (61)	198
—	I (57) ^{<i>f</i>}	314
—	I (65) ^{<i>f</i>}	312

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₈ (Cont'd.)	C ₆ H ₅ CH ₂ CN		50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		n-C ₆ H ₁₃ Br ^r	NaNH ₂
	n-C ₆ H ₉ CH(C ₂ H ₅)CN C ₆ H ₅ CH ₂ CN	(C ₂ H ₅) ₂ N(CH ₂) ₂ Cl (C ₂ H ₅ O) ₂ CH(CH ₂) ₂ Cl n-C ₇ H ₁₅ Br " " n-C ₇ H ₁₅ Br n-C ₇ H ₁₅ OH ^r " " C ₆ H ₅ CH ₂ Cl " " " " " " " "	Li, (C ₂ H ₅) ₂ NH 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂ LDA Na, CH ₃ CO ₂ C ₇ H ₁₅ -n Na, C ₆ H ₅ CO ₂ CH ₃
			NaH " " KOH NaOH 50% aq NaOH,
			Aq NaOH, (n-C ₄ H ₉) ₂ NI 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂ " " " " " " KNH ₂ LICA n-C ₄ H ₉ Li C ₁₀ H ₈ Na Na Mg K Na, CH ₃ CO ₂ CH ₂ C ₆ H ₅ 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	C ₆ H ₅ CH ₂ OH ^r C ₆ H ₅ CHCl ₂ Br(CH ₂) ₂ Br (C ₂ H ₅) ₂ N(CH ₂) ₂ Cl 1-(2-Chloroethyl)piperidine		NaNH ₂ " " " "
	1-(3-Bromopropyl)succinimide		" "
	(C ₂ H ₅ O) ₂ CH(CH ₂) ₂ Cl (C ₂ H ₅) ₂ CBrCO ₂ CH ₃		" " NaH
	3-Chloro-1-ethylpiperidine		NaNH ₂

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

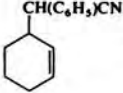
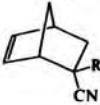
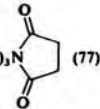
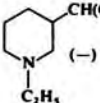
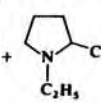
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
-	 (90)	65
Toluene	" (-)	339
NH ₃ , toluene	 I, R = C ₆ H ₁₃ -n (65)	620
" "	I, R = (CH ₂) ₂ N(C ₂ H ₅) ₂ (45)	620
C ₆ H ₆ , HMPA	n-C ₆ H ₉ C(C ₂ H ₅)[(CH ₂) ₂ CH(OC ₂ H ₅) ₂]CN (79)	168
" "	C ₆ H ₅ CH(C ₇ H ₁₅ -n)CN (63)	65,68
C ₆ H ₆	" (-)	607
THF	" (62)	641
" "	" (78) ^r	314
" "	" (73) ^r	310,312
DME	C ₆ H ₅ CH(CH ₂ C ₆ H ₅)CN I, C ₆ H ₅ C(CH ₂ C ₆ H ₅) ₂ CN II	162
HMPA	I (41), II (58)	625
DMF	I (-), II (-)	203
Aq DMSO	I (-), II (26)	96
" "	II (96)	96
" "	I (63), II (14)	592
-	I (86)	227
-	I (60)	606
NH ₃	I (15-30), II (4-35)	597
HMPA	I (-), II (predominant)	625
NH ₃ , Et ₂ O	I (33), II (30)	162
Toluene	I (49), II (11)	162
NH ₃ , Et ₂ O	I (33), II (30)	161
THF, -78°	I (63), II (18)	537
THF	I (12), II (81)	47
THF	I (30), II (25)	198
Et ₂ O	I (63)	642
NH ₃	I (54)	608
HMPA	I (-), II (-)	551
" "	I (85) ^r	309,313,311
" "	[C ₆ H ₅ CH(CN)] ₂ CHC ₆ H ₅ (-)	70
" "	C ₆ H ₅ CH[(CH ₂) ₂ Br]CN (28)	70
C ₆ H ₆	C ₆ H ₅ CH[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN (70)	632
" "	C ₆ H ₅ CH[(CH ₂) ₂ N(CH ₂) ₂]CN (79)	632
Et ₂ O	" (-)	628
C ₆ H ₆ , DMF	 (77)	643
Et ₂ O, C ₆ H ₆	C ₆ H ₅ CH[(CH ₂) ₂ CH(OC ₂ H ₅) ₂]CN (60)	644,645
DMSO	C ₆ H ₅ CH[(C ₂ H ₅) ₂ CO ₂ CH ₃]CN (80)	646
Toluene	 (-) +  (-)	250,251

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₈ (Contd.)	2-ClC ₆ H ₄ CH ₂ CN	C ₆ H ₅ CH ₂ OH*	Na, CH ₃ CO ₂ CH ₂ C ₆ H ₅
	4-ClC ₆ H ₄ CH ₂ CN	C ₆ H ₅ CH ₂ Cl	NaNH ₂
	4-H ₂ NC ₆ H ₄ CH ₂ CN		NaNH ₂
	2,4-Cl ₂ C ₆ H ₃ CH ₂ CN	4-ClC ₆ H ₄ OCH ₂ Cl	NaH
		C ₆ H ₅ CH ₂ Cl	NaNH ₂
		-	-
		(C ₂ H ₅) ₂ N(CH ₂) ₂ Cl	-
	(i-C ₃ H ₇) ₂ CHCN	C ₆ H ₅ O(CH ₂) ₂ Br	LiN(C ₂ H ₅) ₂
	C ₆ H ₅ CH ₂ CN	<i>n</i> -C ₈ H ₁₇ Br*	NaNH ₂
		<i>n</i> -C ₈ H ₁₇ OH*	Na, CH ₃ CO ₂ C ₆ H ₁₁ - <i>n</i>
		<i>i</i> -C ₈ H ₁₇ OH*	Na, C ₆ H ₅ CO ₂ CH ₃
		<i>n</i> -C ₈ H ₁₇ CH(CH ₃)Br	LICA
		<i>n</i> -C ₈ H ₁₇ CH(CH ₃)CH ₂ Br	NaNH ₂
		<i>n</i> -C ₈ H ₁₇ CH(CH ₃)CH ₂ OH*	Na, CH ₃ CO ₂ CH ₂ CH(CH ₃)C ₄ H ₉ - <i>n</i>
		<i>n</i> -C ₈ H ₁₇ CH(CH ₃)CH ₂ OH*	Na, C ₆ H ₅ CO ₂ CH ₃
		C ₆ H ₅ CH(CH ₃)Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	NaNH ₂
		"	KNH ₂
		"	"
		"	"
		L-(+)-C ₆ H ₅ CH(CH ₃)Cl	25% aq NaOH, [(<i>n</i> -C ₈ H ₁₇) ₄ N]Br
		4-CH ₃ C ₆ H ₄ CH ₂ Cl	NaNH ₂
		C ₆ H ₅ (CH ₂) ₂ Br	"
		C ₆ H ₅ (CH ₂) ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		1,4-C ₆ H ₄ (CH ₂ Cl) ₂	C ₁₀ H ₈ Na
		(i-C ₃ H ₇) ₂ N(CH ₂) ₂ Cl	NaNH ₂
	XC ₆ H ₄ CH ₂ CN		
		1-(3-Chloropropyl)-4-methylpiperazine	"
		ClCH ₂ CO ₂ C ₆ H ₁₁	NaOH, [(C ₆ H ₅ CH ₂) ₂ N(C ₂ H ₅) ₂]Br
	2-ClC ₆ H ₄ CH ₂ CN	<i>n</i> -C ₈ H ₁₇ OH*	Na, CH ₃ CO ₂ C ₆ H ₁₁ - <i>n</i>
		"	Na, C ₆ H ₅ CO ₂ CH ₃
	4-ClC ₆ H ₄ CH ₂ CN	<i>n</i> -C ₈ H ₁₇ OH*	Na, CH ₃ CO ₂ C ₆ H ₁₁ - <i>n</i>
		"	Na, C ₆ H ₅ CO ₂ CH ₃

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

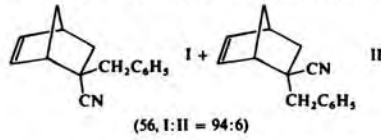
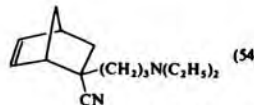
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
-	2-ClC ₆ H ₄ CH(CH ₂ C ₆ H ₅)CN (39) ^r	309,313,311
-	4-ClC ₆ H ₄ CH(CH ₂ C ₆ H ₅)CN (83) ^r	309,313,311
Et ₂ O	4-H ₂ NC ₆ H ₄ C(CH ₂ C ₆ H ₅) ₂ CN (80), 4-(C ₆ H ₅ CH ₂ NH)C ₆ H ₄ C(CH ₂ C ₆ H ₅) ₂ CN (7), 4-[(C ₆ H ₅ CH ₂) ₂ N]C ₆ H ₄ C(CH ₂ C ₆ H ₅) ₂ CN (3)	605
DMF, C ₆ H ₆	(4-ClC ₆ H ₄ O) ₂ CH ₂ (37), [2,3-Cl ₂ C ₆ H ₃ CH(CN)] ₂ CH ₂ (57)	647
C ₆ H ₆	 (56, I:II = 94:6)	177
NH ₃ , toluene	I (39)	620
-	 (54)	620
Et ₂ O	(i-C ₃ H ₇) ₂ C[(CH ₂) ₂ OC ₆ H ₅]CN (25)	562
C ₆ H ₆	C ₆ H ₅ CH(C ₆ H ₁₁ - <i>n</i>)CN I (77)	290,648,607
NH ₃ , Et ₂ O	I (80), C ₆ H ₅ C(C ₆ H ₁₁ - <i>n</i>) ₂ CN (6)	162
-	I (86) ^r	314
-	I (74) ^r	310,312
-	C ₆ H ₅ CH(C ₆ H ₁₁ - <i>i</i>)CN (77) ^r	312
THF, -78°	C ₆ H ₅ CH[CH(CH ₃)C ₆ H ₁₁ - <i>n</i>]CN (82), C ₆ H ₅ C[CH(CH ₃)C ₆ H ₁₁ - <i>n</i>] ₂ CN (2)	537
C ₆ H ₆	C ₆ H ₅ CH[CH ₂ CH(CH ₃)C ₆ H ₉ - <i>n</i>]CN (-)	627
-	" (77) ^r	314
-	" (61) ^r	310
-	<i>erythro</i> -C ₆ H ₅ CH(CH ₃)CH(C ₆ H ₅)CN I, <i>threo</i> -C ₆ H ₅ CH(CH ₃)CH(C ₆ H ₅)CN II	68
-	I + II (66)	65
-	I (-)	649
C ₆ H ₆	I, II (-)	161,650,651
NH ₃ , Et ₂ O	I (99)	161,650
Et ₂ O	I (30), II (29)	650
NH ₃ , THF	I (43), II (33)	652
-	<i>erythro</i> -D(-)-I (88)	653
-	C ₆ H ₅ CH(CH ₂ C ₆ H ₄ CH ₃ -4)CN (95)	654
NH ₃ , Et ₂ O	C ₆ H ₅ CH[(CH ₂) ₂ C ₆ H ₅]CN I (65-71)	162
-	I (61), C ₆ H ₅ C[(CH ₂) ₂ C ₆ H ₅] ₂ CN (16)	65
-	I (35)	198
THF	1,4-C ₆ H ₄ [CH ₂ CH(CN)C ₆ H ₅] ₂ (53)	655
Toluene	XC ₆ H ₄ CH[(CH ₂) ₂ N(C ₆ H ₁₁ - <i>n</i>)] ₂ CN I	
	I, X = H (67)	
	I, X = 2-F (77)	
	I, X = 2-Cl (67)	
	I, X = 2-Br (51)	
	I, X = 4-F (71)	
	I, X = 2-CH ₃ (57)	
	I, X = 2,6-Cl ₂ (74)	
C ₆ H ₆	C ₆ H ₅ CH(CN)(CH ₂) ₂ N(CH ₂) ₂ NCH ₃ (63)	632
C ₆ H ₁₁ OH	C ₆ H ₅ CH(CO ₂ H)CH ₂ CO ₂ H (82) ^r	656
-	2-ClC ₆ H ₄ CH(C ₆ H ₁₁ - <i>n</i>)CN (65) ^r	314
-	" (65) ^r	312
-	4-ClC ₆ H ₄ CH(C ₆ H ₁₁ - <i>n</i>)CN (80) ^r	314
-	" (74) ^r	312

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nu leophile	Electrophile	Base
C ₈ (Cont'd.)	4-ClC ₈ H ₈ CH ₂ CN 2,4-Cl ₂ C ₈ H ₈ CH ₂ CN	C ₆ H ₅ (CH ₂) ₂ Br XC ₆ H ₄ O(CH ₂) ₂ Cl	NaH "
		n-C ₈ H ₁₇ I ⁺	LICA
	C ₈ H ₈ CH ₂ CN	n-C ₉ H ₁₉ OH ⁺ " 1-C ₂ H ₅ CH(CH ₃)(CH ₂) ₂ OH 4-CH ₃ C ₆ H ₄ (CH ₂) ₂ Cl " BrCH ₂ CO ₂ C ₆ H ₁₁ " CH ₃ COC(CO ₂ C ₂ H ₅)(C ₂ H ₅)CH ₂ OH N-(5-Bromopentyl)succinimide " "	Na, CH ₃ CO ₂ C ₉ H ₁₉ ⁿ Na, C ₆ H ₅ CO ₂ CH ₃ Na, CH ₃ CO ₂ (CH ₂) ₂ CH(CH ₃)C ₂ H ₅ ^r NaNH ₂ " 40% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl " KOCH ₃ NaNH ₂ " "
	2,4-Cl ₂ C ₆ H ₃ CH ₂ CN	XC ₆ H ₄ O(CH ₂) ₂ Cl	NaH
	C ₈ H ₈ CH ₂ CN	n-C ₁₀ H ₂₁ OH ⁺ " 1-(3-Chloro-2,2-dimethylpropyl)piperidine " (C ₂ H ₅ O ₂ C) ₂ C(C ₂ H ₅)CH ₂ OH 3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CH ₂ Cl " CH ₂ =CH(CH ₂) ₆ Cl [(C ₂ H ₅) ₂ NCH ₂] ₂ CHCl 1-(Chloromethyl)naphthalene 6-(Chloromethyl)tetralin " N-(3-Bromopropyl)phthalimide	Na, CH ₃ CO ₂ C ₁₀ H ₂₁ ⁿ Na, C ₆ H ₅ CO ₂ CH ₃ NaNH ₂ LiNH ₂ KOCH ₃ NaNH ₂ " " Mg NaNH ₂ " "
	2,4-Cl ₂ C ₆ H ₃ CH ₂ CN C ₈ H ₈ CH ₂ CN	4-CH ₃ OC ₆ H ₄ O(CH ₂) ₂ Cl n-C ₁₂ H ₂₅ OH ⁺ " "	NaH Na, CH ₃ CO ₂ C ₁₂ H ₂₅ ⁿ Na, C ₆ H ₅ CO ₂ CH ₃ " "
		1-Chloroacnaphthene	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
		1-Bromoacnaphthene	NaNH ₂

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

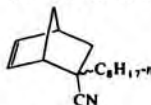
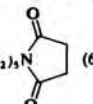
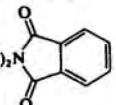
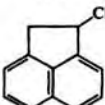
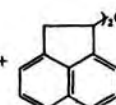
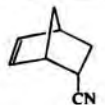
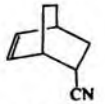

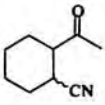
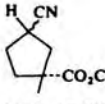
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
DMF, toluene DMF, C ₆ H ₆	4-ClC ₈ H ₈ CH[(CH ₂) ₂ C ₆ H ₅]CN (-) 2,4-Cl ₂ C ₆ H ₃ CH[(CH ₂) ₂ OC ₆ H ₄ X]CN II I, X = H (61) I, X = 4-F (48) I, X = 2-Cl (74) I, X = 4-Cl (66) I, X = 2-Br (94) I, X = 4-Br (98) I, X = 2,4-Cl ₂ (82)	657 647
THF, -78°	 (85)	178
-	C ₆ H ₅ CH(C ₆ H ₁₃ -n)CN (77) ^r " (72) ^r	314 310,312
-	C ₆ H ₅ CH[(CH ₂) ₂ CH(CH ₃)CH ₂ C ₆ H ₄ -r]CN (80) ^r	314
C ₆ H ₆ Toluene	4-CH ₃ C ₆ H ₄ (CH ₂) ₂ CH(C ₆ H ₅)CN (33) " (72)	658 658
-	C ₆ H ₅ CH(CN)CH ₂ CO ₂ C ₆ H ₁₁ (-), C ₆ H ₅ C(CH ₂ CO ₂ C ₆ H ₁₁) ₂ CN (-)	77
CH ₃ OH -	C ₆ H ₅ CH(CN)CH ₂ C(C ₂ H ₅)(CO ₂ C ₂ H ₅)COCH ₃ (27) C ₆ H ₅ CH(CO ₂ H)(CH ₂) ₂ NH ₂ (-) ^r	253 659,660
C ₆ H ₆ , DMF	 (65)	661
DMF, C ₆ H ₆	2,4-Cl ₂ C ₆ H ₃ CH[(CH ₂) ₂ OC ₆ H ₄ X]CN I I, X = H (74) I, X = 4-F (83) I, X = 4-Cl (81) I, X = 2-Br (70) I, X = 4-Br (76) C ₆ H ₅ CH(C ₁₀ H ₂₁ -n)CN (73) ^r " (70) ^r C ₆ H ₅ CH[CH ₂ C(CH ₃) ₂ CH ₂ N(CH ₂) ₃]CN (67) " (76)	647 314 310,312 662 663 253 589
- Toluene CH ₃ OH NH ₃ , Et ₂ O	C ₆ H ₅ CH(CN)CH ₂ C(C ₂ H ₅)(CO ₂ C ₂ H ₅) ₂ (18) 3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CH ₂ CH(C ₆ H ₅)CN (58), [3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CH ₂] ₂ C(C ₆ H ₅)CN (-)	664 665 608
Et ₂ O Toluene	C ₆ H ₅ CH[(CH ₂) ₆ CH=CH ₂]CN (61) C ₆ H ₅ CH[CH(CH ₂ N(C ₂ H ₅) ₂) ₂]CN (54)	664 608
NH ₃ Et ₂ O	C ₆ H ₅ C(CH ₂ C ₁₀ H ₁₉ -1) ₂ CN (42) C ₆ H ₅ CH(CH ₂ C ₁₀ H ₁₁ -6)CN (30)	608 343
C ₆ H ₆ , DMF	 (62)	643
-	2,4-Cl ₂ C ₆ H ₃ CH[(CH ₂) ₂ OC ₆ H ₄ OCH ₂ -4]CN (84) C ₆ H ₅ CH(C ₁₂ H ₂₅ -n)CN (72) ^r " (67) ^r	647 314 310,312
-	 I (67) +  (trace)	81
Et ₂ O	I (-)	666

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₈ (Contd.)		<i>n</i> -C ₁₂ H ₂₃ Br ^f	"
	C ₆ H ₅ CH ₂ CN	<i>n</i> -C ₁₂ H ₂₃ I ^f (C ₆ H ₅) ₂ CHCl " C ₆ H ₅ CH ₂ CH(C ₆ H ₅)Cl [FeCH ₂ N(CH ₃) ₃] ⁺ I ⁻	" LICA KNH ₂ 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl C ₁₀ H ₈ Na NaNH ₂ Na
C ₉	<i>t</i> -C ₄ H ₉ CH(C ₃ H ₇ - <i>i</i>)CN C ₆ H ₅ CH(CH ₃)CN	CH ₃ I " CH ₃ Br CH ₃ I " "	LDA NaNH ₂ " "
	C ₆ H ₅ (CH ₂) ₂ CN 2-CH ₃ C ₆ H ₄ CH ₂ CN 2-NCC ₆ H ₄ CH ₂ CN 3-CH ₃ OC ₆ H ₄ CH ₂ CN 4-CH ₃ OC ₆ H ₄ CH ₂ CN	CH ₃ I " " CH ₃ I " "	LICA KNH ₂ NaOC ₂ H ₅ NaNH ₂ " "
		CH ₂ Cl	"
	<i>t</i> -C ₄ H ₉ CH(C ₃ H ₇ - <i>i</i>)CN C ₆ H ₅ CH(CH ₃)CN	C ₂ H ₅ Br C ₂ H ₅ I C ₂ H ₅ Br " ClCH ₂ OCH ₂ Cl CH ₃ OCH ₂ Cl H ₂ C=CH ₂ 	" LDA NaNH ₂ " 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl " NaNH ₂
	C ₆ H ₅ (CH ₂) ₂ CN 3-CH ₃ OC ₆ H ₄ CH ₂ CN 4-CH ₃ OC ₆ H ₄ CH ₂ CN	C ₂ H ₅ Br ClCH ₂ CN C ₂ H ₅ Br " (CH ₃) ₂ SO ₄ C ₂ H ₅ Cl C ₂ H ₅ Br ^f "	LICA 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl NaNH ₂ " 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl NaNH ₂ "
		C ₂ H ₅ Br	LDA
		C ₂ H ₅ I	LiN(C ₆ H ₁₁) ₂
	<i>i</i> -C ₆ H ₁₃ CH(CH ₃)CN C ₆ H ₅ CH(CH ₃)CN	Cl(CH ₂) ₃ Br <i>n</i> -C ₇ H ₁₅ Br <i>i</i> -C ₇ H ₁₅ Br ^f HC≡CCH ₂ Br CH ₃ OCH(CH ₃)Cl BrCH ₂ CO ₂ CH ₃ <i>i</i> -C ₇ H ₁₅ Br CH ₂ =CHCH ₂ Br	LiN(C ₂ H ₅) ₂ NaNH ₂ " " 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl NaNH ₂ LICA "
	C ₆ H ₅ (CH ₂) ₂ CN	<i>i</i> -C ₇ H ₁₅ Br	LICA

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

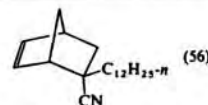
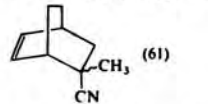
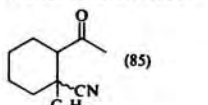
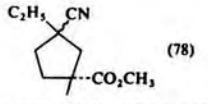
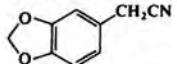
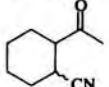


Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NH ₃ , toluene	 (56)	620
THF, -78° NH ₃ , Et ₂ O — THF NH ₃ , Et ₂ O Toluene, DMF	" (-) C ₆ H ₅ CH[CH(C ₆ H ₅) ₂]CN (99) " (94) " (84) C ₆ H ₅ CH[CH(C ₆ H ₅)CH ₂ C ₆ H ₅]CN (80-81) C ₆ H ₅ CH(CH ₂ Fe)CN (35)	178 161 65,85,68 198 249 667
THF, 0° Et ₂ O, NH ₃ C ₆ H ₆ THF, -78° NH ₃ , Et ₂ O C ₂ H ₅ OH Et ₂ O —	<i>t</i> -C ₄ H ₉ C(C ₃ H ₇ - <i>i</i>)(CH ₃)CN (50) C ₆ H ₅ C(CH ₃) ₂ CN (65) " C ₆ H ₅ CH ₂ CH(CH ₃)CN (71), C ₆ H ₅ CH ₂ C(CH ₃) ₂ CN (14) 2-CH ₃ C ₆ H ₄ CH(CH ₃)CN (68) 2-NCC ₆ H ₄ CH(CH ₃)CN (-) 3-CH ₃ OC ₆ H ₄ CH(CH ₃)CN (-) 4-CH ₃ OC ₆ H ₄ CH(CH ₃)CN (47) 4-CH ₃ OC ₆ H ₄ C(CH ₃) ₂ CN (58)	565 581 668 537 669 670 378 671 671
NH ₃	 (61)	588
NH ₃ THF, 0° Toluene C ₆ H ₆ — Et ₂ O	<i>t</i> -C ₄ H ₉ C(C ₂ H ₅)(C ₃ H ₇ - <i>i</i>)CN (56) " (36) C ₆ H ₅ C(CH ₃)(C ₂ H ₅)CN (70) " [C ₆ H ₅ C(CH ₃)(CN)CH ₂] ₂ O (84) C ₆ H ₅ C(CH ₃)(CH ₂ OCH ₃)CN (68) C ₆ H ₅ C(CH ₃)[(CH ₂) ₂ OH]CN (-)	255 565 672 668 72 85 673,674
THF, -78° — C ₆ H ₆ — Et ₂ O, NH ₃ — — —	C ₆ H ₅ CH ₂ CH(C ₂ H ₅)CN (61), C ₆ H ₅ CH ₂ C(C ₂ H ₅) ₂ CN (36) C ₆ H ₅ CH ₂ CH(CH ₃)CN (-) 3-CH ₃ OC ₆ H ₄ CH(C ₂ H ₅)CN (-) 3-CH ₃ OC ₆ H ₄ C(C ₂ H ₅) ₂ CN (-) 4-CH ₃ OC ₆ H ₄ CH(CH ₃)CN (80) 4-CH ₃ OC ₆ H ₄ CH(C ₂ H ₅)CN (85) " (38) 4-CH ₃ OC ₆ H ₄ C(C ₂ H ₅) ₂ CN (61)	537 73 378,675 675 589 570 671 671,675
Et ₂ O, HMPA, -70°	 (85)	111
DME, -78°	 (78)	676
HMPA C ₆ H ₆ — Et ₂ O, C ₆ H ₆ — — THF, -78° —	<i>i</i> -C ₆ H ₁₃ C(CH ₃)[(CH ₂) ₃ Cl]CN (78) C ₆ H ₅ C(CH ₃)(C ₃ H ₇ - <i>n</i>)CN (-) C ₆ H ₅ C(CH ₃)(C ₃ H ₇ - <i>i</i>)CN (60) C ₆ H ₅ C(CH ₃)(CH ₂ C≡CH)CN (60-88) C ₆ H ₅ C(CH ₃)[CH(CH ₃)OCH ₃]CN (68) C ₆ H ₅ C(CH ₃)(CH ₂ CO ₂ CH ₃)CN (-) C ₆ H ₅ CH ₂ CH(C ₃ H ₇ - <i>i</i>)CN (79), C ₆ H ₅ CH ₂ C(C ₃ H ₇ - <i>i</i>) ₂ CN (14) C ₆ H ₅ CH ₂ CH(CH ₂ CH=CH ₂)CN (64), C ₆ H ₅ CH ₂ C(CH ₂ CH=CH ₂) ₂ CN (30)	168 668 583 613 72 677 537 537

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₆ (Contd.)	C ₆ H ₅ (CH ₂) ₂ CN	Cl(CH ₂) ₂ CN	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	XC ₆ H ₄ CH ₂ CN	Cl(CH ₂) ₂ Br	NaNH ₂
			"
			"
			"
			"
	4-CH ₃ OC ₆ H ₄ CH ₂ CN	<i>n</i> -C ₃ H ₇ Br ^f	"
	4-CH ₃ C ₆ H ₄ CH ₂ CN	<i>i</i> -C ₃ H ₇ Br	"
	4-CH ₃ OC ₆ H ₄ CH ₂ CN	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	50% aq NaOH, dicyclohexyl-18-crown-6
	3,4-F(CH ₃ O)C ₆ H ₃ CH ₂ CN	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	NaOH
	2-(2-Pyridyl)butyronitrile	CH ₂ =CHCH ₂ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	2-(4-Pyridyl)butyronitrile	CH ₂ =CHCH ₂ Cl	"
	<i>i</i> -C ₄ H ₉ CH(C ₃ H ₇ - <i>i</i>)CN	<i>i</i> -C ₄ H ₉ Br	NaNH ₂
	C ₆ H ₅ CH(CH ₃)CN	<i>n</i> -C ₄ H ₉ Br	"
		<i>n</i> -C ₄ H ₉ Br	"
		<i>n</i> -C ₄ H ₉ I	"
		<i>i</i> -C ₄ H ₉ Cl	"
		<i>sec</i> -C ₄ H ₉ Cl	"
		<i>t</i> -C ₄ H ₉ Cl	"
		ClCH ₂ CO ₂ C ₂ H ₅	"
		(CH ₃) ₂ N(CH ₂) ₂ Cl ^f	"
		"	LiNH ₂
	4-CH ₃ C ₆ H ₄ CH ₂ CN	ClCH ₂ CH(CH ₃)CH ₂ Br ^f	NaNH ₂
	C ₆ H ₅ (CH ₂) ₂ CN	Cl(CH ₂) ₂ CN	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		<i>n</i> (?) <i>-C</i> ₄ H ₉ Br	LDA
	C ₆ H ₅ (CH ₂) ₂ CN		LICA
	C ₆ H ₅ CH(CH ₃)CN	Cl(CH ₂) ₂ CN	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		<i>n</i> -C ₃ H ₇ Cl	NaNH ₂
		<i>n</i> -C ₃ H ₇ Br	"
		<i>n</i> -C ₃ H ₇ I	"
		<i>i</i> -C ₃ H ₇ Cl	"
		C ₂ H ₅ CH(CH ₃)CH ₂ Cl	"
		<i>n</i> -C ₃ H ₇ CH(CH ₃)Cl	"
		<i>n</i> -C ₃ H ₇ CH(CH ₃)Br	"
		(C ₂ H ₅) ₂ CHCl	"
		<i>t</i> -C ₃ H ₇ Cl	"
			"
		CH ₃ CHClOC ₂ H ₅ - <i>i</i>	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		Br(CH ₂) ₂ CO ₂ C ₂ H ₅	NaNH ₂
		CH ₃ CHBrCO ₂ C ₂ H ₅	"
		BrCH ₂ CO ₂ C ₂ H ₅ - <i>i</i>	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	2-CH ₃ C ₆ H ₄ CH ₂ CN	2-(Chloromethyl)furan	NaH
	4-CH ₃ OC ₆ H ₄ CH ₂ CN	"	NaNH ₂
	C ₆ H ₅ CH(CH ₃)CN	<i>n</i> -C ₆ H ₁₃ Br	"
		(C ₂ H ₅ O) ₂ CHCH ₂ Br	"

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

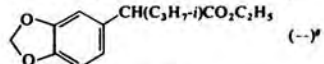
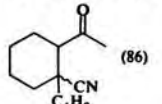
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	C ₆ H ₅ CH ₂ CH[(CH ₂) ₂ CN]CN (73)	73
—	XC ₆ H ₄ CH[(CH ₂) ₂ CN]CN I	
—	I, X = 2-CH ₃ (—)	614
—	I, X = 3-CH ₃ (—)	614
—	I, X = 4-CH ₃ (—)	614
—	I, X = 2-CH ₃ O (—)	614
—	I, X = 4-CH ₃ O (—)	614
—	4-CH ₃ OC ₆ H ₄ C(C ₂ H ₅ - <i>n</i>) ₂ CN (70)	671
Et ₂ O	4-CH ₃ C ₆ H ₄ CH(C ₂ H ₅ - <i>i</i>)CN (—)	673
C ₆ H ₆	4-CH ₃ OC ₆ H ₄ CH(C ₂ H ₅ - <i>i</i>)CN I (ca. 80)	610
—	" (81)	678
—	3,4-F(CH ₃ O)C ₆ H ₃ CH(C ₂ H ₅ - <i>i</i>)CN (—)	678
DMSO	 (—) ^f	679
—	(2-C ₂ H ₅ N)(C ₂ H ₅)(CH ₂ CH=CH ₂)CN (85)	569
—	(4-C ₂ H ₅ N)(C ₂ H ₅)(CH ₂ CH=CH ₂)CN (93)	569
NH ₃	<i>i</i> -C ₄ H ₉ C(C ₃ H ₇ - <i>i</i>)(C ₂ H ₅ - <i>i</i>)CN (39), <i>t</i> -C ₄ H ₉ (<i>i</i> -C ₃ H ₇)C=C=NC ₄ H ₉ - <i>i</i> (12)	255
Toluene	C ₆ H ₅ C(CH ₃)(C ₄ H ₉ - <i>n</i>)CN (61)	166
Toluene or C ₆ H ₆	" (61)	166,668
C ₆ H ₆	" (56)	649
Toluene	" (62)	166
—	C ₆ H ₅ C(CH ₃)(C ₄ H ₉ - <i>i</i>)CN (60-69)	166
Toluene	C ₆ H ₅ C(CH ₃)(C ₄ H ₉ - <i>sec</i>)CN (67-68)	166
—	C ₆ H ₅ C(CH ₃)(C ₄ H ₉ - <i>t</i>)CN (4-12)	166
Et ₂ O	C ₆ H ₅ C(CH ₃)(CH ₂ CO ₂ C ₂ H ₅)CN (—)	680
C ₆ H ₆	C ₆ H ₅ C(CH ₃)[(CH ₂) ₂ N(CH ₃) ₂]CN (81)	681
Toluene	" (55)	663
—	4-CH ₃ C ₆ H ₄ CH[CH ₂ CH(CH ₃)CH ₂ Cl]CN (—)	614
—	C ₆ H ₅ CH ₂ CH[(CH ₂) ₂ CN]CN (—)	73
Et ₂ O, HMPA, -70°	 (86)	111
THF, -78°	C ₆ H ₅ CH ₂ CH(C ₂ H ₅)CN (76), C ₆ H ₅ CH ₂ C(C ₂ H ₅) ₂ CN (12)	537
—	C ₆ H ₅ CH ₂ CH[(CH ₂) ₂ CN]CN (—)	73
—	C ₆ H ₅ C(CH ₃)(C ₃ H ₇ - <i>n</i>)CN (77-78)	167
—	" (76)	167,668
—	" (60)	167
—	C ₆ H ₅ C(CH ₃)(C ₃ H ₇ - <i>i</i>)CN (84-85)	167
—	C ₆ H ₅ C(CH ₃)[CH ₂ CH(CH ₃)C ₂ H ₅]CN (90)	167
—	C ₆ H ₅ C(CH ₃)[CH(CH ₃)C ₃ H ₇ - <i>n</i>]CN (69)	167
—	" (84)	167
—	C ₆ H ₅ C(CH ₃)[CH(C ₂ H ₅) ₂]CN (84-88)	167
—	C ₆ H ₅ C(CH ₃)(C ₃ H ₇ - <i>t</i>)CN (trace)	167
—	C ₆ H ₅ C(CH ₃)(C ₃ H ₉)CN (86-90)	167
—	C ₆ H ₅ C(CH ₃)[CH(CH ₃)OC ₂ H ₅ - <i>i</i>]CN (75)	72
C ₆ H ₆	C ₆ H ₅ C(CH ₃)[(CH ₂) ₂ CO ₂ C ₂ H ₅]CN (—)	682
Et ₂ O	C ₆ H ₅ C(CH ₃)[CH(CH ₃)CO ₂ C ₂ H ₅]CN (64)	683-685
—	C ₆ H ₅ C(CH ₃)(CH ₂ CO ₂ C ₂ H ₅ - <i>i</i>)CN (74)	78
DMF	(2-C ₂ H ₅ O)CH ₂ CH(C ₆ H ₄ CH ₃ -2)CN (—)	634
—	(2-C ₂ H ₅ O)CH ₂ CH(C ₆ H ₄ OCH ₃ -4)CN (—)	635
C ₆ H ₆	C ₆ H ₅ C(CH ₃)(C ₆ H ₁₃ - <i>n</i>)CN (—)	668
Et ₂ O	C ₆ H ₅ C(CH ₃)[CH ₂ CH(OC ₂ H ₅) ₂]CN (65-68)	686,637,638

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₉ (Contd.)	(C ₂ H ₅ O) ₂ CHCH ₂ Br	4-(2-Chloroethyl)morpholine	NaNH ₂
		C ₂ H ₅ CHBrCO ₂ C ₂ H ₅ BrCH ₂ CO ₂ C ₄ H ₉ -t	" 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		1-(2-Chloroethyl)pyrrolidine	NaNH ₂
	(CH ₃) ₂ C=CH(CH ₂) ₂ CH(CH ₃)CN		LiN(C ₂ H ₅) ₂
	2-CH ₂ OC ₆ H ₄ CH ₂ CN 2-(NC) ₆ H ₄ CH ₂ CN C ₆ H ₅ CH(CH ₃)CN	C ₆ H ₅ CH ₂ Cl C ₆ H ₅ CH ₂ Cl' n-C ₈ H ₁₇ Br C ₆ H ₅ CH ₂ Cl (C ₂ H ₅ O) ₂ CH(CH ₂) ₂ Cl (C ₂ H ₅ O) ₂ CHCH(CH ₃)Br 1-(2-chloroethyl)piperidine n-C ₈ H ₁₇ CHBrCO ₂ C ₂ H ₅	NaH NaOC ₂ H ₅ NaNH ₂ 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂ " " "
	C ₆ H ₅ (CH ₂) ₂ CN		LICA
	4-CH ₂ C ₆ H ₄ CH ₂ CN 2-NCC ₆ H ₄ CH ₂ CN	C ₆ H ₅ CH ₂ Cl C ₆ H ₅ (CH ₂) ₂ Cl 2-NCC ₆ H ₄ CH ₂ Cl' C ₆ H ₅ (CH ₂) ₂ I	" NaNH ₂ NaOC ₂ H ₅ "
	C ₆ H ₅ CH(CH ₃)CN	n-C ₈ H ₁₇ Br BrCH ₂ CO ₂ C ₆ H ₁₁ n-C ₈ H ₁₇ CHBrCO ₂ C ₂ H ₅ (C ₂ H ₅ O) ₂ CHCH(CH ₃)Br n-C ₈ H ₁₇ X	NaNH ₂ 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂ " LICA
	C ₆ H ₅ (CH ₂) ₂ CN	n-C ₆ H ₁₃ CH(CH ₃)Br	"
	C ₆ H ₅ CH(CH ₃)CN 4-CH ₂ OC ₆ H ₄ CH ₂ CN	(C ₂ H ₅ O) ₂ CHCH(CH ₃ -n)Br 3,4,5-(CH ₂ O) ₃ C ₆ H ₂ CH ₂ Cl	NaNH ₂ "
C ₆ H ₅ CH(CH ₃)CN	(C ₂ H ₅ O) ₂ CHCH(C ₆ H ₄ -n)Br 6-(Chloromethyl)tetralin	" "	
C ₁₀	1,2-C ₆ H ₄ (CH ₂ CN) ₂	CH ₃ I (2 eq)	CH ₃ Li
		" (4 eq)	"
		" (4 eq)	"
	1,3-C ₆ H ₄ (CH ₂ CN) ₂	" (2 eq)	"
	" (4 eq)	"	"
	1,4-C ₆ H ₄ (CH ₂ CN) ₂	" (2 eq)	"
	" (4 eq)	"	"
	4-C ₂ H ₅ OC ₆ H ₄ CH ₂ CN	CH ₃ Cl CH ₃ I'	NaOH NaNH ₂
	3,4-(CH ₂ O) ₂ C ₆ H ₃ CH ₂ CN	"	t-C ₄ H ₉ OK

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)




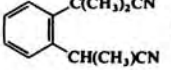
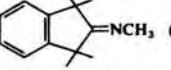
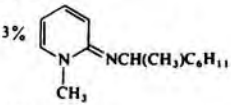
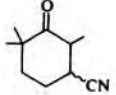
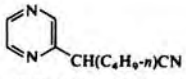
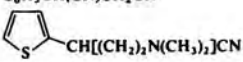
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ H ₆	C ₆ H ₅ C(CH ₃)(CN)(CH ₂) ₂ N  (69)	681
Et ₂ O	C ₆ H ₅ C(CH ₃)[CH(C ₂ H ₅)CO ₂ C ₂ H ₅]CN (48)	683,685,687
-	C ₆ H ₅ C(CH ₃)(CH ₂ CO ₂ C ₄ H ₉ -t)CN (76)	78
-	 -C(CH ₂ CH=CH ₂)[(CH ₂) ₂ N(CH ₃) ₂]CN (22)	567
HMPA	(CH ₃) ₂ C=CH(CH ₂) ₂ C(CH ₃)(CN)(CH ₂) ₂ O  (80)	556
DMSO	2-CH ₂ OC ₆ H ₄ CH(CH ₂ C ₆ H ₅)CN (77)	688
C ₂ H ₅ OH	2-(NC) ₆ H ₄ CH(CH ₂ C ₆ H ₅)CN (-)	670
C ₆ H ₆	C ₆ H ₅ C(CH ₃)(C ₂ H ₅ -n)CN (-)	668
-	C ₆ H ₅ C(CH ₃)(CH ₂ C ₆ H ₅)CN (82)	68
Et ₂ O, C ₆ H ₆	C ₆ H ₅ C(CH ₃)[(CH ₂) ₂ CH(OC ₂ H ₅) ₂]CN (70)	644,645
Et ₂ O	C ₆ H ₅ C(CH ₃)[CH(CH ₃)CH(OC ₂ H ₅) ₂]CN (69)	689,685
C ₆ H ₆	C ₆ H ₅ C(CH ₃)[(CH ₂) ₂ N(CH ₃) ₂]CN (72)	681
Et ₂ O	C ₆ H ₅ C(CH ₃)[CH(C ₂ H ₅ -n)CO ₂ C ₂ H ₅]CN (49)	683,685,687
THF, -78°	C ₆ H ₅ CH ₂ CH(C ₂ H ₅)CN (67), C ₆ H ₅ CH ₂ C(C ₂ H ₅) ₂ CN (1)	537
"	(C ₆ H ₅ CH ₂) ₂ CHCN (70), (C ₆ H ₅ CH ₂) ₂ CCN (24)	537
C ₆ H ₆ or toluene	4-CH ₂ C ₆ H ₄ CH[(CH ₂) ₂ C ₆ H ₅]CN (38-40)	658
C ₂ H ₅ OH	2-NCC ₆ H ₄ CH(CH ₂ C ₆ H ₅ -2-CN)CN (-)	670
-	2-NCC ₆ H ₄ CH[(CH ₂) ₂ C ₆ H ₅]CN (-)	670
C ₆ H ₆	C ₆ H ₅ C(CH ₃)(C ₆ H ₅ -n)CN (66)	649,668
-	C ₆ H ₅ C(CH ₃)(CH ₂ CO ₂ C ₆ H ₁₁)CN (78)	78
Et ₂ O	C ₆ H ₅ C(CH ₃)[CH(C ₂ H ₅ -n)CO ₂ C ₂ H ₅]CN (38)	683,687,685
-	C ₆ H ₅ C(CH ₃)[CH(C ₂ H ₅)CH(OC ₂ H ₅) ₂]CN (55)	689,685
THF, -78°	C ₆ H ₅ CH ₂ CH(C ₆ H ₅ -n)CN I, C ₆ H ₅ CH ₂ C(C ₆ H ₅ -n) ₂ CN II X = Cl: I (63), II (36) X = Br: I (63), II (37) X = I: I (70), II (30)	537
-	C ₆ H ₅ CH ₂ CH[CH(CH ₃)C ₆ H ₁₃ -n]CN (85)	537
-	C ₆ H ₅ CH ₂ C[CH(CH ₃)C ₆ H ₁₃ -n] ₂ CN (1)	689,685
Et ₂ O	C ₆ H ₅ C(CH ₃)[CH(C ₂ H ₅ -n)CH(OC ₂ H ₅) ₂]CN (52)	689,685
NH ₃ , Et ₂ O	4-CH ₂ OC ₆ H ₄ CH[CH ₂ C ₆ H ₅ (OCH ₂) ₂ -3,4,5]CN (68)	589
-	4-CH ₂ OC ₆ H ₄ C[CH ₂ C ₆ H ₅ (OCH ₂) ₂ -3,4,5] ₂ CN (-)	689,685
Et ₂ O	C ₆ H ₅ C(CH ₃)[CH(C ₂ H ₅ -n)CH(OC ₂ H ₅) ₂]CN (47)	689,685
-	C ₆ H ₅ C(CH ₃)(CH ₂ C ₁₀ H ₁₁ -6)CN (33)	343
Et ₂ O, THF, -100°	1,2-C ₆ H ₄ [CH(CH ₃)CN] ₂ (94)	45
" (15 min)	 I (90)	45
" (20 hr)	I (72),  (28)	45
"	1,3-C ₆ H ₄ [CH(CH ₃)CN] ₂ (92)	45
"	1,3-C ₆ H ₄ [C(CH ₃) ₂ CN] ₂ (99)	45
"	1,4-C ₆ H ₄ [CH(CH ₃)CN] ₂ (80), 1,4-C ₆ H ₄ [C(CH ₃) ₂ CN] ₂ (10)	45
"	1,4-C ₆ H ₄ [C(CH ₃) ₂ CN] ₂ (99)	45
"	" (87)	690
Aq DMSO	4-C ₂ H ₅ OC ₆ H ₄ CH(CH ₃)CN (63)	671
-	4-C ₂ H ₅ OC ₆ H ₄ C(CH ₃) ₂ CN (64)	671
t-C ₄ H ₉ OH	3,4-(CH ₂ O) ₂ C ₆ H ₃ CH(CH ₃)CN (-), 3,4-(CH ₂ O) ₂ C ₆ H ₃ C(CH ₃) ₂ CN (-)	258

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₀ (Cont'd.)	2-(CH ₃ OCH ₂ O)C ₆ H ₄ CH ₂ CN	CH ₃ I	NaNH ₂
	2,5-(CH ₃) ₂ C ₆ H ₃ CH ₂ CN	"	"
	C ₆ H ₃ CH(C ₂ H ₅)CN	CH ₃ Br	50% aq NaOH.
			3% 
		CH ₃ I	NaNH ₂
		"	NaH
		CH ₂ Cl ₂	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		CH ₂ Br ₂ ^c	"
		CH ₃ I	LDA
		"	NaNH ₂
	<i>i</i> -C ₄ H ₉ COCH ₂ CH(C ₂ H ₅)CN	C ₂ H ₅ Br	LDA
	3-(C ₂ H ₅ O)C ₆ H ₄ CH ₂ CN	"	NaNH ₂
	4-(C ₂ H ₅ O)C ₆ H ₄ CH ₂ CN	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	NaNH ₂
		"	"
	4-CH ₃ COC ₆ H ₄ CH ₂ CN	"	"
	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN	"	NaOC ₂ H ₅
		"	NaNH ₂
		"	<i>i</i> -C ₄ H ₉ OK
		C ₂ H ₅ I	NaNH ₂
		(CH ₃) ₂ SO ₄	"
	2,5-(CH ₃) ₂ C ₆ H ₃ CH ₂ CN	C ₂ H ₅ Br ^c	"
	C ₆ H ₃ CH(C ₂ H ₅)CN	Cl(CH ₂) ₂ Cl	"
		Br(CH ₂) ₂ Br	"
		C ₂ H ₅ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		H ₂ C=O	NaNH ₂
		"	"
		"	"
	4-ClC ₆ H ₄ CH(C ₂ H ₅)CN	"	"
	C ₆ H ₃ CH(CN)CH ₂ CN	ClCH ₂ CN	"
		C ₂ H ₅ Br ^c	"
	C ₆ H ₃ CH(C ₂ H ₅)CN	<i>n</i> -C ₂ H ₅ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	"
		<i>i</i> -C ₃ H ₇ Br	"
		CH ₂ =CHCH ₂ Br	"
		HC≡CCH ₂ Br	NaNH ₂
		Cl(CH ₂) ₂ Br	"
		"	LiN(C ₂ H ₅) ₂
		"	NaNH ₂
		Br(CH ₂) ₂ Br	"
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

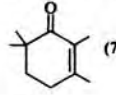
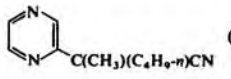
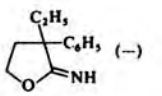
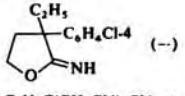
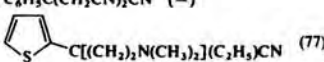
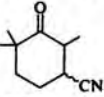
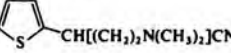
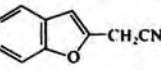
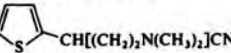
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	2-(CH ₃ OCH ₂ O)C ₆ H ₄ C(CH ₃) ₂ CN (90)	688
Et ₂ O or C ₆ H ₆	2,5-(CH ₃) ₂ C ₆ H ₃ CH(CH ₃)CN (67)	649
—	C ₆ H ₃ C(CH ₃)(C ₂ H ₅)CN (69)	592
Et ₂ O	" (85) ^b	691
—	" (67)	692
—	C ₆ H ₃ C(C ₂ H ₅)(CH ₂ Cl)CN (—)	693
—	C ₆ H ₃ C(C ₂ H ₅)(CH ₂ Br)CN (71)	693-695
Et ₂ O, HMPA, -70°	 (75) ^a	111
NH ₃ , dioxane	 (—)	272
Et ₂ O, HMPA, -70°	<i>i</i> -C ₄ H ₉ COCH ₂ C(C ₂ H ₅) ₂ CN (76)	111
—	3-C ₂ H ₅ OC ₆ H ₄ C(C ₂ H ₅) ₂ CN (—)	675
—	4-C ₂ H ₅ OC ₆ H ₄ CH(C ₂ H ₅)CN (—)	696
—	" (60)	671
—	4-C ₂ H ₅ OC ₆ H ₄ C(C ₂ H ₅) ₂ CN (70)	671
Et ₂ O	4-(CH ₃ CO)C ₆ H ₄ CH(C ₂ H ₅)CN (85)	697
C ₂ H ₅ OH	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH(C ₂ H ₅)CN (82)	698
DME	" (91)	699
<i>i</i> -C ₄ H ₉ OH	" (—)	258
C ₆ H ₆	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH(CH ₃)CN (59)	589
Et ₂ O or C ₆ H ₆	2,5-(CH ₃) ₂ C ₆ H ₃ CH(C ₂ H ₅)CN (75)	649
C ₆ H ₆	C ₆ H ₃ C(C ₂ H ₅)[(CH ₂) ₂ Cl]CN (50)	599
—	C ₆ H ₃ C(C ₂ H ₅)[(CH ₂) ₂ Br]CN (6)	599
—	C ₆ H ₃ C(C ₂ H ₅) ₂ CN (70)	66
Et ₂ O	C ₆ H ₃ C(C ₂ H ₅)[(CH ₂) ₂ OH]CN (—)	673,674
NH ₃	 (—)	179
"	 (—)	179
Et ₂ O	C ₆ H ₃ C(CH ₂ CN) ₂ CN (—)	603
—	 C[(CH ₂) ₂ N(CH ₃) ₂](C ₂ H ₅)CN (77)	567
C ₆ H ₆	C ₆ H ₃ C(C ₂ H ₅)(C ₂ H ₅ - <i>n</i>)CN (73)	583
—	" (59)	66
—	C ₆ H ₃ C(C ₂ H ₅)(C ₂ H ₅ - <i>i</i>)CN (43)	66
—	C ₆ H ₃ C(C ₂ H ₅)(CH ₂ CH=CH ₂)CN (93)	66
Et ₂ O, C ₆ H ₆	C ₆ H ₃ C(C ₂ H ₅)(CH ₂ C≡CH)CN (60-88)	613
C ₆ H ₆	C ₆ H ₃ C(C ₂ H ₅)[(CH ₂) ₂ Cl]CN I (56), [C ₆ H ₃ C(C ₂ H ₅)(CN)CH ₂] ₂ CH ₂ II (30)	700
Et ₂ O	I (68)	557
C ₆ H ₆	I (56)	701,702
—	I (54), II (29)	700
—	C ₆ H ₃ C(C ₂ H ₅)(CH ₂ CH=CH ₂)CN (—), C ₆ H ₃ C(C ₂ H ₅)[(CH ₂) ₂ Br]CN (—), [C ₆ H ₃ C(C ₂ H ₅)(CN)CH ₂] ₂ CH ₂ (negligible)	693

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₀ (Contd.)	(C ₆ H ₅ CH(C ₂ H ₅)CN	BrCH ₂ CO ₂ CH ₃	NaNH ₂
	4-C ₂ H ₅ C ₆ H ₄ CH ₂ CN	Cl(CH ₂) ₂ Br	"
	2,3-(CH ₃) ₂ C ₆ H ₃ CH ₂ CN	<i>i</i> -C ₃ H ₇ Br	"
	2,5-(C ₂ H ₅ O)(Cl)C ₆ H ₃ CH ₂ CN	<i>n</i> -C ₃ H ₇ Br	"
	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN	<i>i</i> -C ₃ H ₇ Br	"
	2,5-(CH ₃) ₂ C ₆ H ₃ CH ₂ CN	<i>n</i> -C ₃ H ₇ Br	"
		<i>i</i> -C ₃ H ₇ Br	"
	4-F ₂ CHCF ₂ OC ₆ H ₄ CH ₂ CN	"	50% aq NaOH, dicyclohexyl-18-crown-6
	1,4-C ₆ H ₄ (CH ₂ CN) ₂	CH ₂ =CHCH ₂ Br	NaH
		Cl(CH ₂) ₂ Br	LDA
		RX ^c	NaNH ₂
	2-(2-Pyridyl)-4-pentenitrile	CH ₂ =CHCH ₂ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		<i>n</i> -C ₃ H ₇ Cl	NaNH ₂
		<i>i</i> -C ₃ H ₇ Cl	"
	2-(4-Pyridyl)valeronitrile	CH ₂ =CHCH ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	<i>i</i> -C ₃ H ₇ I	47% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
2-CH ₃ O ₂ CC ₆ H ₄ CH ₂ CN	<i>n</i> -C ₄ H ₉ Br	LICA	
1,4-C ₆ H ₄ (CH ₂ CN) ₂	<i>i</i> -C ₄ H ₉ Br	NaH	
2,5-(CH ₃) ₂ C ₆ H ₃ CH ₂ CN	<i>n</i> -C ₄ H ₉ Br	NaNH ₂	
	<i>sec</i> -C ₄ H ₉ Br	"	
C ₆ H ₅ CH(C ₂ H ₅)CN	<i>n</i> -C ₄ H ₉ Cl	"	
	"	NaH	
	<i>n</i> -C ₄ H ₉ Br	NaNH ₂	
	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
	<i>sec</i> -C ₄ H ₉ Cl	NaNH ₂	
	"	NaH	
	<i>i</i> -C ₄ H ₉ Cl	NaNH ₂	
	"	NaH	
	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
	<i>i</i> -C ₄ H ₉ Cl	NaNH ₂	
	Cl(CH ₂) ₄ Cl	"	
	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
	"	NaNH ₂	
	Cl(CH ₂) ₄ Br	LiN(C ₂ H ₅) ₂	
	Br(CH ₂) ₄ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
	I(CH ₂) ₄ CN	NaNH ₂	
	(CH ₂) ₄ N(CH ₂) ₂ Cl	"	
C ₆ H ₅ CH(CN)CH ₂ CN	BrCH ₂ CO ₂ C ₂ H ₅	"	
	RX ^c	"	
2,5-(CH ₃) ₂ C ₆ H ₃ CH ₂ CN	<i>n</i> -C ₅ H ₁₁ Br	NaNH ₂	
C ₆ H ₅ CH(C ₂ H ₅)CN	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
	<i>i</i> -C ₅ H ₁₁ Br	"	
	Cl(CH ₂) ₂ Cl	NaNH ₂	
	Br(CH ₂) ₂ Br	"	
	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

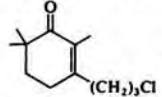
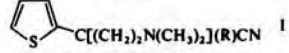
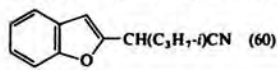
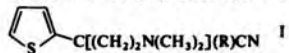
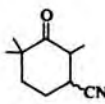
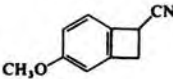
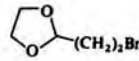
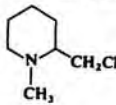
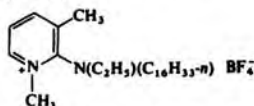
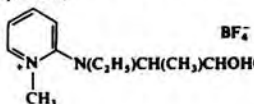
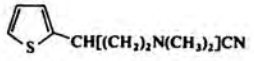
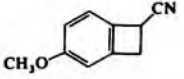
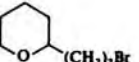
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	C ₆ H ₅ C(C ₂ H ₅)(CH ₂ CO ₂ CH ₃)CN (—)	677
—	4-C ₂ H ₅ C ₆ H ₄ CH[(CH ₂) ₂ Cl]CN (—)	614
Toluene	2,3-(CH ₃) ₂ C ₆ H ₃ CH(C ₂ H ₅ - <i>o</i>)CN (80)	703
NH ₃	2,5-(C ₂ H ₅ O)(Cl)C ₆ H ₃ CH(C ₂ H ₅ - <i>n</i>)CN (—)	704
DME	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH(C ₂ H ₅ - <i>o</i>)CN (91)	699
Et ₂ O or C ₆ H ₆	2,5-(CH ₃) ₂ C ₆ H ₃ CH(C ₂ H ₅ - <i>n</i>)CN (53)	649
"	2,5-(CH ₃) ₂ C ₆ H ₃ CH(C ₂ H ₅ - <i>o</i>)CN (70)	649
C ₆ H ₆	4-F ₂ CHCF ₂ OC ₆ H ₄ CH(C ₂ H ₅ - <i>o</i>)CN (74)	678
DMSO	1,4-C ₆ H ₄ [CH(CH ₂ CH=CH ₂)CN] ₂ (33)	705
Et ₂ O, HMPA, -70°	 (73)	111
—	 I	567
	I, R = C ₂ H ₅ - <i>i</i> (71)	
	I, R = CH ₂ C≡CH (54)	
—	(2-C ₂ H ₅ N)C(CH ₂ CH=CH ₂) ₂ CN (92)	569
Et ₂ O	(2-C ₂ H ₅ N)C(CH ₂ CH=CH ₂)(C ₂ H ₅ - <i>n</i>)CN (71)	572
"	(2-C ₂ H ₅ N)C(CH ₂ CH=CH ₂)(C ₂ H ₅ - <i>i</i>)CN (62)	572
—	(4-C ₂ H ₅ N)C(C ₂ H ₅ - <i>n</i>)(CH ₂ CH=CH ₂)CN (89)	569
—	 CH(C ₂ H ₅ - <i>o</i>)CN (60)	706
THF, -78°	2-CH ₃ O ₂ CC ₆ H ₄ CH(C ₂ H ₅ - <i>n</i>)CN (79)	707
DMSO	1,4-C ₆ H ₄ [CH(C ₂ H ₅ - <i>o</i>)CN] ₂ (27)	705
Et ₂ O or C ₆ H ₆	2,5-(CH ₃) ₂ C ₆ H ₃ CH(C ₂ H ₅ - <i>n</i>)CN (77)	649
"	2,5-(CH ₃) ₂ C ₆ H ₃ CH(C ₂ H ₅ - <i>sec</i>)CN (82)	649
Toluene	C ₆ H ₅ C(C ₂ H ₅)(C ₂ H ₅ - <i>n</i>)CN (87)	42
"	" (73-86)	42
C ₆ H ₆	" (63)	649
—	" (26)	66
Toluene	C ₆ H ₅ C(C ₂ H ₅)(C ₂ H ₅ - <i>sec</i>)CN (93)	42
"	" (77-80)	42
Toluene	C ₆ H ₅ C(C ₂ H ₅)(C ₂ H ₅ - <i>i</i>)CN (90)	42
"	" (80)	42
—	" (40)	66
Toluene	C ₆ H ₅ C(C ₂ H ₅)(C ₂ H ₅ - <i>t</i>)CN (8)	42
C ₆ H ₆	C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₄ Cl]CN I (44)	701,702
—	I (65)	693
Et ₂ O	I (44), [C ₆ H ₅ C(C ₂ H ₅)(CN)CH ₂ CH ₂] ₂ II (41)	700
—	I (68)	549
—	C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₄ Br]CN (47), II (—)	693-695
Toluene, Et ₂ O	C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₂ CN]CN (—)	708
—	C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₂ N(CH ₂) ₂]CN (61)	599
Et ₂ O	C ₆ H ₅ C(CH ₂ CO ₂ C ₂ H ₅)(CN)CH ₂ CN (62)	603
—	 I	
	I, R = C ₂ H ₅ - <i>n</i> (30) ^p	567
	I, R = (CH ₂) ₄ Cl (—)	567
	I, R = CH ₂ CO ₂ C ₂ H ₅ , X = Br (52)	568
Et ₂ O or C ₆ H ₆	2,5-(CH ₃) ₂ C ₆ H ₃ CH(C ₂ H ₅ - <i>n</i>)CN (63)	649
—	C ₆ H ₅ C(C ₂ H ₅)(C ₂ H ₅ - <i>n</i>)CN (52)	66
	C ₆ H ₅ C(C ₂ H ₅)(C ₂ H ₅ - <i>o</i>)CN (62)	66
C ₆ H ₆	C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₂ Cl]CN (48),	700-702
	[C ₆ H ₅ C(C ₂ H ₅)(CN)(CH ₂) ₂ CH ₂] ₂ I (33)	
—	C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₂ Br]CN (40), I (44)	700
—	C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₂ Br]CN (49), I (23)	693-695

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₀ (Contd.)	C ₆ H ₅ CH(C ₂ H ₅)CN	CH ₃ CHBrCO ₂ C ₂ H ₅ Br(CH ₂) ₂ CO ₂ C ₂ H ₅	NaNH ₂ "
		<i>i</i> -C ₃ H ₇ Br	LDA
			NaNH ₂
	1,4-C ₆ H ₄ (CH ₂ CN) ₂ 1,3-C ₆ H ₄ (CH ₂ CN) ₂ 2,5-(CH ₂) ₂ C ₆ H ₃ CH ₂ CN C ₆ H ₅ CH(C ₂ H ₅)CN	C ₆ H ₁₁ Br " <i>n</i> -C ₆ H ₁₃ Br " Br(CH ₂) ₆ Br (C ₂ H ₅ O) ₂ CHCH ₂ Br (C ₂ H ₅) ₂ N(CH ₂) ₂ Cl " " ClCH ₂ CO ₂ C ₆ H ₄ - <i>t</i> C ₂ H ₅ CHBrCO ₂ C ₂ H ₅ BrCH ₂ CH ₂ CO ₂ C ₂ H ₅ - <i>i</i>	NaNH " NaNH ₂ 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂ " " LiNH ₂ 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl " NaNH ₂ NaOH, dimethylpiperidinium sulfate
	2,5-(CH ₂ O) ₂ C ₆ H ₃ CH ₂ CN		NaNH ₂
	C ₆ H ₅ CH(C ₂ H ₅)CN	<i>n</i> -C ₇ H ₁₅ Br C ₆ H ₅ CH ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl or 30% aq KOH, [(CH ₂ =CHCH ₂) ₂ N(CH ₃) ₂]SO ₄ 50% aq NaOH,  BF ₄ ⁻ " 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl 50% aq NaOH,  BF ₄ ⁻
		C ₆ H ₅ CH ₂ Cl	NaNH ₂
	2-(2-Pyridyl)-4-pentenitrile	C ₆ H ₅ CH ₂ Cl	"
			"
	C ₆ H ₅ CH(C ₂ H ₅)CN	C ₆ H ₅ O(CH ₂) ₂ Br (C ₂ H ₅ O) ₂ CH(C ₂ H ₅)Br <i>n</i> -C ₆ H ₁₃ CHBrCO ₂ C ₂ H ₅ C ₆ H ₅ CO ₂ (CH ₂) ₂ Br (C ₂ H ₅ O) ₂ CHCH(C ₂ H ₅ - <i>n</i>)Br	" " " " "

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

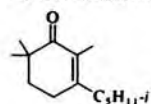
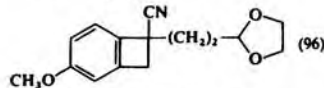
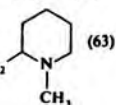

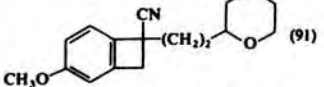
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₂ O C ₆ H ₆	C ₆ H ₅ C(C ₂ H ₅)[CH(CH ₃)CO ₂ C ₂ H ₅]CN (53) C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₂ CO ₂ C ₂ H ₅]CN (-)	683-685 682
Et ₂ O, HMPA, -70°	 (79) ^a	111
NH ₃	 (96)	173
DMSO "	1,4-C ₆ H ₄ [CH(C ₆ H ₁₁)CN] ₂ (47) 1,3-C ₆ H ₄ [CH(C ₆ H ₁₁)CN] ₂ (-)	705 705
Et ₂ O or C ₆ H ₆ "	2,5-(CH ₂) ₂ C ₆ H ₃ CH(C ₆ H ₁₃ - <i>n</i>)CN (74) C ₆ H ₅ C(C ₂ H ₅)(C ₆ H ₁₃ - <i>n</i>)CN (86)	649 66
C ₆ H ₆ "	C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₆ Br]CN (39), [C ₆ H ₅ C(C ₂ H ₅)(CN)(CH ₂) ₂] ₂ (29) C ₆ H ₅ C(C ₂ H ₅)[CH ₂ CH(OC ₂ H ₅) ₂]CN (76)	700-702 709,686, 638,637 599
- Toluene "	C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN (53) " (58) " (41)	663 66
- "	C ₆ H ₅ C(C ₂ H ₅)(CH ₂ CO ₂ C ₆ H ₄ - <i>t</i>)CN (77) C ₆ H ₅ C(C ₂ H ₅)[CH(C ₂ H ₅)CO ₂ C ₂ H ₅]CN (63) C ₆ H ₅ C(C ₂ H ₅)(CO ₂ H)CH ₂ CH ₂ CO ₂ H (-) ^a	78,85 683-685 710
C ₆ H ₆	 (63)	711
-	C ₆ H ₅ C(C ₂ H ₅)(C ₇ H ₁₅ - <i>n</i>)CN (66)	66
-	C ₆ H ₅ C(CH ₂ C ₆ H ₅)(C ₂ H ₅)CN (81)	592
-	" (94) " (100)	66,85,68 592
-	 (61)	567
Et ₂ O	(2-C ₅ H ₄ N)C(CH ₂ CH=CH ₂)(CH ₂ C ₆ H ₅)CN (54)	572
NH ₃	 (91)	713
- Et ₂ O " C ₆ H ₆ , DMF Et ₂ O	C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₂ OC ₂ H ₅]CN (56) C ₆ H ₅ C(C ₂ H ₅)[CH(C ₂ H ₅)(OC ₂ H ₅) ₂]CN (60) C ₆ H ₅ C(C ₂ H ₅)[CH(C ₆ H ₄ - <i>n</i>)CO ₂ C ₂ H ₅]CN (60-65) C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₂ OCOC ₂ H ₅]CN (38) C ₆ H ₅ C(C ₂ H ₅)[CH(C ₂ H ₅ - <i>n</i>)CH(OC ₂ H ₅) ₂]CN (49)	599 689,685 712,683,685 714,715 689,685

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₀ (Contd.)			NaNH ₂
	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN	3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CH ₂ Cl	"
	C ₆ H ₅ CH(C ₂ H ₅)CN C ₆ H ₅ CH(C ₂ H ₅)CN	(C ₂ H ₅ O) ₂ CHCH(C ₄ H _{9-n})Br C ₆ H ₅ CH ₂ N(CH ₃)(CH ₂) ₂ Cl	" "
	C ₆ H ₅ CH(C ₂ H ₅)CN	<i>N</i> -(3-Bromopropyl)phthalimide	"
		<i>i</i> -C ₈ H ₁₃ C(CH ₃)(CN)(CH ₂) ₂ Cl	LiN(C ₂ H ₅) ₂
C ₆ H ₅ CH(C ₂ H ₅)CN	1-Chloroacenaphthene	"	
	1-Bromoacenaphthene (C ₆ H ₅) ₂ CHBr ^r	NaNH ₂ "	
		"	
3,4-(Cl)(C ₂ H ₅ O) ₂ C ₆ H ₃ CH ₂ CN	3,4-(CH ₃ O) ₂ C ₆ H ₃ (CH ₂) ₂ N(CH ₃)(CH ₂) ₂ Cl	"	
		NaH	
2-(CH ₃ OCH ₂ O) ₂ C ₆ H ₄ CH ₂ CN	(C ₆ H ₅ CH ₂) ₂ N(CH ₂) ₂ Cl	"	
4-(<i>n</i> -C ₃ H ₇ O) ₂ C ₆ H ₄ CH ₂ CN	CH ₃ I ^r	NaNH ₂	
C ₆ H ₅ CH(C ₃ H _{7-i})CN	CH ₃ I	NaH	
	CH ₃ Cl	LiN(C ₂ H ₅) ₂	
	CH ₃ I	"	
	C ₂ H ₅ Br	NaNH ₂	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NH ₃		169,170
NH ₃ , Et ₂ O	1. R ¹ = OCH ₃ , R ² = H (75) I. R ¹ = H, R ² = OCH ₃ (76)	
Et ₂ O	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH[CH ₂ C ₆ H ₃ (OCH ₃) ₂ -3,4,5]CN (66), 3,4-(CH ₃ O) ₂ C ₆ H ₃ Cl[CH ₂ C ₆ H ₃ (OCH ₃) ₂ -3,4,5]CN (-)	589
-	C ₆ H ₅ C(C ₂ H ₅)[CH(C ₄ H _{9-n})CH(OC ₂ H ₅) ₂]CN (45) C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₂ N(CH ₃)CH ₂ C ₆ H ₅]CN (-)	689,685 599
C ₆ H ₆ , DMF		643,716
HMPA		168
-		81
Et ₂ O	" (-)	666
-	C ₆ H ₅ C(C ₂ H ₅)[CH(C ₆ H ₅) ₂]CN (97)	66
NH ₃ , THF		174,175
Toluene	3,4-(Cl)(C ₂ H ₅ O) ₂ C ₆ H ₃ CH[(CH ₂) ₂ N(CH ₃)(CH ₂) ₂ C ₆ H ₃ (OCH ₃) ₂ -3,4]CN (69)	717
DMF		171
DMSO	2-(CH ₃ OCH ₂ O) ₂ C ₆ H ₄ CH[(CH ₂) ₂ N(CH ₂ C ₆ H ₅) ₂]CN (75)	688
-	4-(<i>n</i> -C ₃ H ₇ O) ₂ C ₆ H ₄ CH(CH ₃)CN (53)	671
-	4-(<i>n</i> -C ₃ H ₇ O) ₂ C ₆ H ₄ C(CH ₃) ₂ CN (67)	671
-	C ₆ H ₅ C(CH ₃)(C ₃ H _{7-i})CN (40)	692
DME		176,718
"	I: II = 81:19 (82-96) I: II = 72:28 (91)	176,718
NH ₃		719

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₁ (Contd.)		"	LDA
	4-(<i>n</i> -C ₇ H ₁₅ O)C ₆ H ₄ CH ₂ CN	C ₂ H ₅ I'	NaNH ₂
	3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CH ₂ CN	(CH ₃) ₂ SO ₄	"
	3-CH ₃ OC ₆ H ₄ CH(C ₂ H ₅)CN	Cl(CH ₂) ₂ Cl	"
	C ₆ H ₅ CH(C ₃ H _{7-<i>n</i>)CN}	H ₂ C=CH ₂	"
	C ₆ H ₅ CH(C ₃ H _{7-<i>i</i>)CN}	CH ₃ OCH ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
	4-(<i>i</i> -C ₃ H ₇)C ₆ H ₄ CH ₂ CN	H ₂ C=CH ₂	NaNH ₂
		Cl(CH ₂) ₂ Br	"
	<i>t</i> -C ₄ H ₉ 	[(CH ₃) ₂ O]BF ₄	LiN(C ₂ H ₅) ₂
	3-CH ₃ OC ₆ H ₄ CH(C ₂ H ₅)CN	<i>i</i> -C ₃ H ₇ Br	NaNH ₂
	C ₆ H ₅ CH(C ₃ H _{7-<i>n</i>)CN}	H ₂ C=CHCH ₃	"
		HC≡CCH ₂ Br	"
		Cl(CH ₂) ₂ Br	"
	2-(4-Pyridyl)hexanenitrile	"	"
		CH ₂ =CHCH ₂ Cl	"
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
	3-CH ₃ OC ₆ H ₄ CH(C ₂ H ₅)CN	<i>sec</i> -C ₄ H ₉ Br	NaNH ₂
	C ₆ H ₅ CH(C ₃ H _{7-<i>n</i>)CN}	C ₂ H ₅ O(CH ₂) ₂ Cl	"
		BrCH ₂ CO ₂ C ₂ H ₅	"
		Br(CH ₂) ₂ CO ₂ C ₂ H ₅	"
		CH ₃ CHBrCO ₂ C ₂ H ₅	"
	C ₆ H ₅ CH(C ₃ H _{7-<i>i</i>)CN}	(CH ₃) ₂ NCH(CH ₃)CH ₂ Cl	"
			"
	C ₆ H ₅ CH(C ₃ H _{7-<i>n</i>)CN}		C ₁₀ H ₈ Na
		(C ₂ H ₅ O) ₂ CHCH ₂ Br	NaNH ₂
		BrCH ₂ CO ₂ C ₄ H _{9-<i>t</i>}	"
		C ₃ H ₇ CHBrCO ₂ C ₂ H ₅	"
	C ₆ H ₅ CH(C ₃ H _{7-<i>i</i>)CN}	4-(2-Chloroethyl)morpholine	"
	C ₆ H ₅ CH(C ₃ H _{7-<i>n</i>)CN}	BrCH ₂ CO ₂ C ₄ H _{9-<i>t</i>}	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
		C ₆ H ₅ CH ₂ Cl	"

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₂ O, HMPA, -70°		111
—	4-(<i>n</i> -C ₇ H ₁₅ O)C ₆ H ₄ CH(C ₂ H ₅)CN (52)	671
—	4-(<i>n</i> -C ₇ H ₁₅ O)C ₆ H ₄ C(C ₂ H ₅) ₂ CN (60)	671
C ₆ H ₆	3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CH(CH ₃)CN (62)	589
"	3-CH ₃ OC ₆ H ₄ C(C ₂ H ₅)[(CH ₂) ₂ Cl]CN (43)	720
Et ₂ O	C ₆ H ₅ C(C ₃ H _{7-<i>n</i>)[(CH₂)₂OH]CN (-)}	673,674
—	C ₆ H ₅ C(C ₃ H _{7-<i>i</i>)[(CH₂)₂OH]CN (7)}	72
Et ₂ O	C ₆ H ₅ C(C ₃ H _{7-<i>i</i>)[(CH₂)₂OH]CN (-)}	673,674
—	4-(<i>i</i> -C ₃ H ₇)C ₆ H ₄ CH[(CH ₂) ₂ Cl]CN (-)	614
DME		176
	I:II = ~42:58 (24-28)	
—	3-CH ₃ OC ₆ H ₄ C(C ₂ H ₅)(C ₃ H _{7-<i>n</i>)CN (-)}	675
Et ₂ O	C ₆ H ₅ C(C ₃ H _{7-<i>n</i>)[(CH₂)₂OH]CN (70)'}	720
Et ₂ O, C ₆ H ₆	C ₆ H ₅ C(C ₃ H _{7-<i>n</i>)(CH₂C≡CH)CN (60-88)}	613
C ₆ H ₆	C ₆ H ₅ C(C ₃ H _{7-<i>n</i>)[(CH₂)₂Cl]CN (-)}	721
—	(4-C ₃ H ₄ N)C(C ₆ H _{4-<i>n</i>)(CH₂CH=CH₂)CN (93)}	569
—	(4-C ₃ H ₄ N)C(C ₆ H _{4-<i>i</i>)(CH₂CH=CH₂)CN (91)}	569
—		569
—	3-CH ₃ OC ₆ H ₄ C(C ₂ H ₅)(C ₄ H _{9-<i>sec</i>)CN (-)}	675
C ₆ H ₆	C ₆ H ₅ C(C ₃ H _{7-<i>n</i>)[(CH₂)₂OC₂H₅]CN (58)}	720
"	C ₆ H ₅ C(C ₃ H _{7-<i>n</i>)(CH₂CO₂C₂H₅)CN (-)}	722
"	C ₆ H ₅ C(C ₃ H _{7-<i>n</i>)[(CH₂)₂CO₂C₂H₅]CN (-)}	682
C ₆ H ₆ or Et ₂ O	C ₆ H ₅ C(C ₃ H _{7-<i>n</i>)[(CH₂)₂CO₂C₂H₅]CN (42)}	683-685, 720
C ₆ H ₆	C ₆ H ₅ C(C ₃ H _{7-<i>i</i>)[(CH₂CH(CH₃)N(CH₃)₂]CN (-)}	723
NH ₃		172,724
THF		198
Et ₂ O	C ₆ H ₅ C(C ₃ H _{7-<i>n</i>)[CH₂CH(OC₂H₅)₂]CN (78-80)}	686,637,725a
—	C ₆ H ₅ C(C ₃ H _{7-<i>n</i>)(CH₂CO₂C₄H_{9-<i>t</i>)CN (74)}}	78
Et ₂ O	C ₆ H ₅ C(C ₃ H _{7-<i>n</i>)[CH(C₂H₅)CO₂C₂H₅]CN (51)}	683-685
C ₆ H ₆	C ₆ H ₅ C(C ₃ H _{7-<i>i</i>)(CN)(CH₂)₂N}	681
—	C ₆ H ₅ C(C ₃ H _{7-<i>i</i>)(CH₂CO₂C₄H_{9-<i>t</i>)CN (56)}}	78
—	C ₆ H ₅ C(C ₃ H _{7-<i>n</i>)(CH₂C₄H₉)CN (69)}	68

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₁ (Contd.)	C ₆ H ₅ CH(C ₃ H _{7-n})CN	(C ₂ H ₅ O) ₂ CH(CH ₂) ₂ Cl	NaNH ₂
		(C ₂ H ₅ O) ₂ CHCH(CH ₃)Br	"
		<i>n</i> -C ₇ H ₇ CHBrCO ₂ C ₂ H ₅	"
		<i>N</i> -(3-Bromopropyl)succinimide	"
	C ₆ H ₅ CH(C ₃ H _{7-i})CN 2-Quinolyacetonitrile C ₆ H ₅ CH(C ₃ H _{7-n})CN	C ₆ H ₅ CH ₂ Cl	50% aq NaOH. [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		C ₆ H ₅ CH ₂ OH ⁺	Na. CH ₃ CO ₂ CH ₂ C ₆ H ₅
		(C ₂ H ₅ O) ₂ CHCH(C ₂ H ₅)Br	NaNH ₂
		<i>n</i> -C ₄ H ₉ CHBrCO ₂ C ₂ H ₅	"
		C ₆ H ₅ CO ₂ (CH ₂) ₂ Br	"
	3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CH ₂ CN	(C ₂ H ₅ O) ₂ CH(C ₃ H _{7-n})Br	"
3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CH ₂ Cl		"	
C ₆ H ₅ CH(C ₃ H _{7-n})CN	(C ₂ H ₅ O) ₂ CHCH(C ₄ H _{9-n})Br	"	
	6-(Chloromethyl)tetralin	"	
	<i>N</i> -(3-Bromopropyl)phthalimide	"	
C ₆ H ₅ CH(C ₃ H _{7-i})CN	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHCl	"	
	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ N(CH ₃)(CH ₂) ₂ Cl	"	
	3,4-(CH ₃ O) ₂ C ₆ H ₃ (CH ₂) ₂ N(CH ₃)(CH ₂) ₂ Cl	"	
		"	
C ₁₂		CH ₃ I	NaH
		CH ₃ I ⁺	NaNH ₂
			
		CH ₃ I	NaH
			50% aq NaOH. [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
			<i>i</i> -C ₃ H ₇ ONa
			NaNH ₂
			CH ₃ Li
			50% aq NaOH. [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	2-Naphthylacetonitrile	CH ₂ Br ₂	NaNH ₂
		CH ₃ I	"
	Cyanomethylferrocene		<i>n</i> -C ₄ H ₉ Li
	CH ₃ I	NaNH ₂	
	CH ₃ I	"	
4-(<i>i</i> -C ₄ H ₉)C ₆ H ₄ CH ₂ CN	C ₂ H ₅ Br	50% aq NaOH. [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
3-CH ₃ OC ₆ H ₄ CH(C ₃ H _{7-n})CN	Cl(CH ₂) ₂ Cl	NaNH ₂	
	Br(CH ₂) ₂ Br	"	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

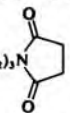
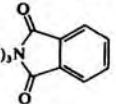
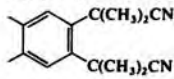
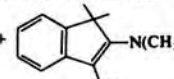
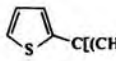
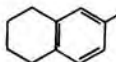
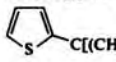
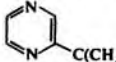

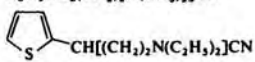
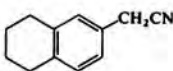


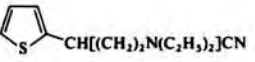
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₂ O, C ₆ H ₆	C ₆ H ₅ C(C ₃ H _{7-n})[(CH ₂) ₂ CH(OC ₂ H ₅) ₂]CN (75)	644,645
Et ₂ O	C ₆ H ₅ C(C ₃ H _{7-n})[CH(CH ₃)CH(OC ₂ H ₅) ₂]CN (48)	689,685
"	C ₆ H ₅ C(C ₃ H _{7-n})[CH(C ₃ H _{7-n})CO ₂ C ₂ H ₅]CN (62)	683-685
C ₆ H ₆ , DMF	C ₆ H ₅ C(C ₃ H _{7-n})(CN)(CH ₂) ₂ N  (45)	643
—	C ₆ H ₅ C(C ₃ H _{7-i})(CH ₂ C ₆ H ₅)CN (39)	68
—	(2-C ₆ H ₅ N)CH(CH ₂ C ₆ H ₅)CN (54) ⁺	309,313
Et ₂ O	C ₆ H ₅ C(C ₃ H _{7-n})[CH(C ₂ H ₅)CH(OC ₂ H ₅) ₂]CN (51)	689,685
"	C ₆ H ₅ C(C ₃ H _{7-n})[CH(C ₄ H _{9-n})CO ₂ C ₂ H ₅]CN (60-65)	712,683,685
C ₆ H ₆ , DMF	C ₆ H ₅ C(C ₃ H _{7-n})[(CH ₂) ₂ OCO ₂ C ₆ H ₅]CN (34)	714,715
Et ₂ O	C ₆ H ₅ C(C ₃ H _{7-n})[CH(C ₃ H _{7-n})(OC ₂ H ₅) ₂]CN (61)	689,685
NH ₃ , Et ₂ O	3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CH(CN)CH ₂ C ₆ H ₅ (OCH ₃) ₂ -3,4,5 (50), 3,4,5-(CH ₃ O) ₃ C ₆ H ₂ C(CN)[CH ₂ C ₆ H ₅ (OCH ₃) ₂ -3,4,5] ₂ (-)	589
Et ₂ O	C ₆ H ₅ C(C ₃ H _{7-n})[CH(C ₄ H _{9-n})CH(OC ₂ H ₅) ₂]CN (42)	689,685
Et ₂ O	C ₆ H ₅ C(C ₃ H _{7-n})(CH ₂ C ₁₀ H ₁₁ -6)CN (38)	343
C ₆ H ₆ , DMF	C ₆ H ₅ C(C ₃ H _{7-n})(CN)(CH ₂) ₂ N  (58)	643,716
Toluene	C ₆ H ₅ C(C ₃ H _{7-i})[CH(CH ₂ N(C ₂ H ₅) ₂)]CN (-)	665
"	C ₆ H ₅ C(C ₃ H _{7-i})[(CH ₂) ₂ N(CH ₃)C ₆ H ₅ (OCH ₃) ₂ -3,4]CN (-)	725b
"	C ₆ H ₅ C(C ₃ H _{7-i})[(CH ₂) ₂ N(CH ₃)(CH ₂) ₂ C ₆ H ₅ (OCH ₃) ₂ -3,4]CN (76)	717
DMSO	 (-) +  (-)	726
—	 C[(CH ₂) ₂ N(C ₂ H ₅) ₂](CH ₃)CN (63)	567
Et ₂ O or C ₆ H ₆	 CH(CH ₃)CN (56)	727
DMF	1-C ₁₀ H ₇ CH(CH ₃)CN I, 1-C ₁₀ H ₇ C(CH ₃) ₂ CN II	634
	I (-)	97
	I (92)	97
	II (64)	97
C ₆ H ₆	I (41)	584
Et ₂ O	I (98)	728-730
"	II (94)	729
Et ₂ O, THF	II (95)	44
—	(1-C ₁₀ H ₇ CH(CN)) ₂ CH ₂ (80)	97
C ₆ H ₆	2-C ₁₀ H ₇ CH(CH ₃)CN (91)	729
"	2-C ₁₀ H ₇ C(CH ₃) ₂ CN (74)	729
Et ₂ O	FeC(CH ₃) ₂ CN (60)	49
—	 C[(CH ₂) ₂ N(CH ₃) ₂](CH ₃)CN (87)	567
Dioxane	 C(CH ₃)(C ₆ H ₅)CN (76)	731
—	4- <i>i</i> -C ₄ H ₉ C ₆ H ₄ CH(C ₂ H ₅)CN (-)	696
C ₆ H ₆	3-CH ₃ OC ₆ H ₄ C(C ₃ H _{7-n})[(CH ₂) ₂ Cl]CN (50)	720
"	3-CH ₃ OC ₆ H ₄ C(C ₃ H _{7-n})[(CH ₂) ₂ Br]CN (43)	720

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₂ (Contd.)	3-CH ₃ OC ₆ H ₄ CH(C ₂ H _{7-n})CN		NaNH ₂
	4-CH ₃ C ₆ H ₄ CH(C ₂ H _{7-n})CN	"	"
	C ₆ H ₅ CH(C ₄ H _{9-n})CN	"	"
	C ₆ H ₅ CH(C ₄ H _{9-i})CN	C ₂ H ₅ Br	"
	C ₆ H ₅ CH(CH ₂ CO ₂ C ₂ H ₅)CN	ClCH ₂ CN	"
	C ₆ H ₅ CH[(CH ₂) ₂ N(CH ₃) ₂]CN	C ₂ H ₅ Br	"
	 CH[(CH ₂) ₂ N(CH ₃) ₂]CN	RX'	"
	1-Naphthylacetonitrile	C ₂ H ₅ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(CH ₃) ₂]Cl
	"	"	NaNH ₂
	"	C ₂ H ₅ Br Cl(CH ₂) ₂ Cl (CH ₃) ₂ SO ₄	<i>i</i> -C ₃ H ₇ ONa
2-Naphthylacetonitrile	C ₂ H ₅ Br	NaNH ₂	
	"	"	
	"	"	
4-(<i>i</i> -C ₄ H ₉)C ₆ H ₄ CH ₂ CN	Cl(CH ₂) ₂ Br	"	
3-CH ₃ OC ₆ H ₄ CH(C ₂ H _{7-n})CN		"	
C ₆ H ₅ CH(C ₄ H _{9-n})CN	<i>i</i> -C ₃ H ₇ Br Br(CH ₂) ₂ Cl	NaH NaNH ₂	
C ₆ H ₅ CH(C ₄ H _{9-i})CN	<i>i</i> -C ₃ H ₇ Br	"	
C ₆ H ₅ CH(C ₄ H _{9-sec})CN	CH ₂ =CHCH ₂ Br	"	
C ₆ H ₅ CH(C ₄ H _{9-sec})CN	CH ₃ S(CH ₂) ₂ Cl	"	
C ₆ H ₅ CH[(CH ₂) ₂ N(CH ₃) ₂]CN	Cl(CH ₂) ₂ Br Cl(CH ₂) ₂ Cl Br(CH ₂) ₂ Br <i>i</i> -C ₃ H ₇ Br	" " " "	
 CH[(CH ₂) ₂ N(CH ₃) ₂]CN	RX'	"	
1-Naphthylacetonitrile	<i>n</i> -C ₃ H ₇ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(CH ₃) ₂]Cl	
"	"	NaNH ₂	
"	"	"	
"	<i>i</i> -C ₃ H ₇ Br	"	
"	"	"	
"	CH ₂ =CHCH ₂ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(CH ₃) ₂]Cl NaNH ₂	
"	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(CH ₃) ₂]Cl	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

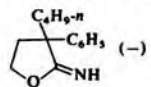

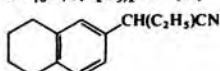

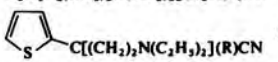
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₂ O	3-CH ₃ OC ₆ H ₄ C(C ₂ H _{7-n})[(CH ₂) ₂ OH]CN (8) ^y	720
"	4-CH ₃ C ₆ H ₄ C(C ₂ H _{7-i})[(CH ₂) ₂ OH]CN (-)	673,674
NH ₃	 (-)	179
Et ₂ O	C ₆ H ₅ C(C ₂ H ₅)(C ₄ H _{9-i})CN (50)	343
"	C ₆ H ₅ C(CH ₂ CO ₂ C ₂ H ₅)(CH ₂ CN)CN (42)	603
C ₆ H ₆	C ₆ H ₅ C(C ₂ H ₅)[(CH ₂) ₂ N(CH ₃) ₂]CN (85)	681
-	 C[(CH ₂) ₂ N(CH ₃) ₂](R)CN I	567
	I R = C ₂ H ₅ (63) I R = (CH ₂) ₂ Cl (53) ^y	
-	1-C ₁₀ H ₇ CH(C ₂ H ₅)CN I. 1-C ₁₀ H ₇ C(C ₂ H ₅) ₂ CN II	
	I (82)	97
	II (31)	97
Et ₂ O	I (96)	728,729
Et ₂ O	II (96)	732,729,730
"	[1-C ₁₀ H ₇ CH(CN)CH ₂] ₂ (47)	733
C ₆ H ₆	1-C ₁₀ H ₇ CH(CH ₃)CN (31)	584
"	2-C ₁₀ H ₇ CH(C ₂ H ₅)CN (87)	729
"	2-C ₁₀ H ₇ C(C ₂ H ₅) ₂ CN (76)	729
Et ₂ O or C ₆ H ₆	 CH(C ₂ H ₅)CN (45)	727
	 C(C ₂ H ₅)(CN)(CH ₂) ₂ N(CH ₃) ₂ (72)	567
-	4- <i>i</i> -C ₄ H ₉ C ₆ H ₄ CH[(CH ₂) ₂ Cl]CN (-)	614
Et ₂ O	3-CH ₃ OC ₆ H ₄ C(C ₂ H _{7-n})[CH ₂ CH(OH)CH ₃]CN (72) ^y	620
"	C ₆ H ₅ C(C ₄ H _{9-n})(C ₂ H _{7-i})CN (76)	692
C ₆ H ₆	C ₆ H ₅ C(C ₄ H _{9-n})[(CH ₂) ₂ Cl]CN (-)	721
Et ₂ O	C ₆ H ₅ C(C ₄ H _{9-i})(C ₂ H _{7-i})CN (50)	343
"	C ₆ H ₅ C(C ₄ H _{9-i})(CH ₂ CH=CH ₂)CN (50)	343
Xylene	C ₆ H ₅ C(C ₄ H _{9-sec})[(CH ₂) ₂ SCH ₃]CN (-)	734
Toluene	C ₆ H ₅ C[(CH ₂) ₂ N(CH ₃) ₂][(CH ₂) ₂ Cl]CN (68) ^y	735
"	" (24) ^y	735
Et ₂ O	C ₆ H ₅ C[(CH ₂) ₂ N(CH ₃) ₂][(CH ₂) ₂ Br]CN (26) ^y	735
C ₆ H ₆	C ₆ H ₅ C[(CH ₂) ₂ N(CH ₃) ₂](C ₂ H _{7-i})CN (90)	681
-	 C[(CH ₂) ₂ N(CH ₃) ₂](R)CN I	567
	I R = C ₂ H _{7-i} (98)	
	I R = CH ₂ CH=CH ₂ (45)	
	I R = CH ₂ C≡CH (27)	
-	1-C ₁₀ H ₇ CH(C ₂ H _{7-n})CN (90)	97
Et ₂ O	" (94)	728,729
"	1-C ₁₀ H ₇ C(C ₂ H _{7-n}) ₂ CN (92)	732,729
"	1-C ₁₀ H ₇ CH(C ₂ H _{7-i})CN II (93)	728-730
"	1-C ₁₀ H ₇ C(C ₂ H _{7-i}) ₂ CN (90)	729
"	II (83)	97
Et ₂ O	1-C ₁₀ H ₇ CH(CH ₂ CH=CH ₂)CN III (96)	736,728,729
"	1-C ₁₀ H ₇ C(CH ₂ CH=CH ₂) ₂ CN IV (90)	729
-	III (88)	97
	IV (80)	97

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₂ (Contd.)	1-Naphthylacetonitrile	HC≡CCH ₂ Br ^r	NaNH ₂
	2-Naphthylacetonitrile	<i>i</i> -C ₂ H ₅ Br	"
		"	"
		CH ₂ =CHCH ₂ Br	"
		RX ^r	"
		HC≡CCH ₂ Cl ^r	"
	C ₆ H ₅ CH(C ₆ H ₅ - <i>n</i>)CN	<i>n</i> -C ₄ H ₉ I	NaH
	C ₆ H ₅ CH(C ₆ H ₅ - <i>i</i>)CN	<i>n</i> -C ₄ H ₉ Br	NaNH ₂
	C ₆ H ₅ CH(C ₆ H ₅ - <i>sec</i>)CN	<i>i</i> -C ₄ H ₉ Br	"
	C ₆ H ₅ CH[(CH ₂) ₂ N(CH ₂) ₂]CN	<i>sec</i> -C ₄ H ₉ Br	"
		Cl(CH ₂) ₄ Br	"
	C ₆ H ₅ CH(CH ₂ CO ₂ C ₂ H ₅)CN	BrCH ₂ CO ₂ C ₂ H ₅	"
		RX ^r	"
	Cyanomethylferrocene	<i>n</i> -C ₄ H ₉ Br	<i>n</i> -C ₄ H ₉ Li
	1-Naphthylacetonitrile	"	NaNH ₂
		"	"
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(CH ₂) ₂]Cl
		<i>i</i> -C ₄ H ₉ Br ^r	NaNH ₂
		<i>sec</i> -C ₄ H ₉ Br ^r	"
		CH ₂ CH=CHCH ₂ Br ^r	"
		(CH ₂) ₂ N(CH ₂) ₂ Cl	"
	2-Naphthylacetonitrile	<i>n</i> -C ₄ H ₉ Br	"
		"	"
		<i>i</i> -C ₄ H ₉ Br	50% aq NaOH, dicyclohexyl-18-crown-6
		<i>sec</i> -C ₄ H ₉ Br	"
		<i>n</i> -C ₄ H ₉ Br ^r	NaNH ₂
		RX ^r	"
		BrCH ₂ CO ₂ C ₂ H ₅	"
	4- <i>i</i> -C ₄ H ₉ C ₆ H ₄ CH ₂ CN	2-(Chloromethyl)furan	NaH
	3-CH ₂ OC ₆ H ₄ CH(C ₂ H ₅ - <i>n</i>)CN	CH ₂ CHBrCO ₂ C ₂ H ₅	NaNH ₂
	C ₆ H ₅ CH(C ₆ H ₅ - <i>n</i>)CN	"	"
	C ₆ H ₅ CH(C ₆ H ₅ - <i>i</i>)CN	<i>n</i> -C ₂ H ₅ Cl	"
	1-Naphthylacetonitrile	<i>i</i> -C ₂ H ₅ Br	"
		"	"
		(CH ₂) ₂ N(CH ₂) ₂ Cl	"
		(CH ₂) ₂ NCH ₂ CH(CH ₂)Cl	"
		C ₂ H ₅ N(CH ₂)(CH ₂) ₂ Cl	"
		2-(Chloromethyl)furan	"
			"

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

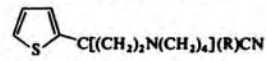
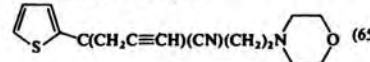
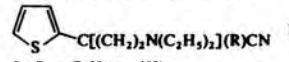
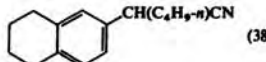
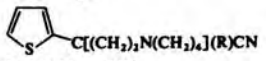
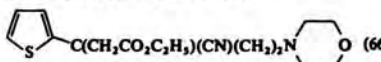
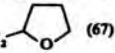
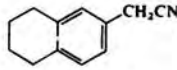

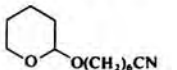
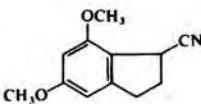
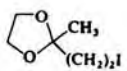
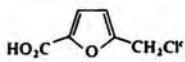
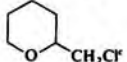
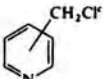
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₂ O NH ₃ , toluene C ₆ H ₆	1-C ₁₀ H ₇ CH(CH ₂ C≡CH)CN (32)	736
	2-C ₁₀ H ₇ CH(C ₂ H ₅ - <i>i</i>)CN (94)	737,738
"	" (91)	729
"	2-C ₁₀ H ₇ C(C ₂ H ₅ - <i>i</i>) ₂ CN (82)	729
"	2-C ₁₀ H ₇ CH(CH ₂ CH=CH ₂)CN (82)	729
—		567
	R = C ₂ H ₅ - <i>i</i> (74)	
	R = CH ₂ CH=CH ₂ (78)	
—		567
HMPA	C ₆ H ₅ C(C ₆ H ₅ - <i>n</i>) ₂ CN (—)	625
Et ₂ O	C ₆ H ₅ C(C ₆ H ₅ - <i>i</i>)(C ₆ H ₅ - <i>n</i>)CN (50)	343
C ₆ H ₆	C ₆ H ₅ C(C ₆ H ₅ - <i>sec</i>)(C ₆ H ₅ - <i>i</i>)CN (45)	343
"	C ₆ H ₅ C[(CH ₂) ₂ N(CH ₂) ₂](C ₆ H ₅ - <i>sec</i>)CN (88)	681
Et ₂ O	C ₆ H ₅ C[(CH ₂) ₂ N(CH ₂) ₂][(CH ₂) ₄ Cl]CN (—)	739
"	C ₆ H ₅ C(CH ₂ CO ₂ C ₂ H ₅) ₂ CN (68)	603
—		567
	I R = C ₆ H ₅ - <i>n</i> (63)	
	I R = CH ₂ CO ₂ C ₂ H ₅ , X = Br (62)	
Et ₂ O	FeCl(C ₆ H ₅ - <i>n</i>) ₂ CN (56)	49
"	1-C ₁₀ H ₇ CH(C ₆ H ₅ - <i>n</i>)CN (95)	728,729
"	1-C ₁₀ H ₇ C(C ₆ H ₅ - <i>n</i>) ₂ CN (71)	664,729,732
—	1-C ₁₀ H ₇ CH(C ₆ H ₅ - <i>n</i>)CN (91)	97
Et ₂ O	1-C ₁₀ H ₇ CH(C ₆ H ₅ - <i>i</i>)CN (92)	728,729
"	1-C ₁₀ H ₇ C(C ₆ H ₅ - <i>i</i>) ₂ CN (89)	732,729
"	1-C ₁₀ H ₇ CH(C ₆ H ₅ - <i>sec</i>)CN (94)	728,729
"	1-C ₁₀ H ₇ CH(CH ₂ CH=CHCH ₂)CN (93)	728,729,736
"	1-C ₁₀ H ₇ CH[(CH ₂) ₂ N(CH ₂) ₂]CN (92)	740,621
C ₆ H ₆	2-C ₁₀ H ₇ CH(C ₆ H ₅ - <i>n</i>)CN (80)	729
"	2-C ₁₀ H ₇ C(C ₆ H ₅ - <i>n</i>) ₂ CN (78)	729
—	2-C ₁₀ H ₇ CH(C ₆ H ₅ - <i>i</i>)CN (79)	738,737
—	2-C ₁₀ H ₇ CH(C ₆ H ₅ - <i>sec</i>)CN (86)	738,737
Et ₂ O or C ₆ H ₆		727
—		567
	R = C ₆ H ₅ - <i>n</i> (56)	
	R = CH ₂ CO ₂ C ₂ H ₅ , X = Br (60)	
Et ₂ O		567
DMF	4- <i>i</i> -C ₄ H ₉ C ₆ H ₄ CH[CH ₂ (C ₆ H ₅ -O-2)]CN (—)	634
C ₆ H ₆	3-CH ₂ OC ₆ H ₄ C(C ₂ H ₅ - <i>n</i>)[CH(CH ₂)CO ₂ C ₂ H ₅]CN (55)	720
Et ₂ O	C ₆ H ₅ C(C ₆ H ₅ - <i>n</i>)[CH(CH ₂)CO ₂ C ₂ H ₅]CN (44)	683,685
"	C ₆ H ₅ C(C ₆ H ₅ - <i>i</i>)(C ₂ H ₅ - <i>n</i>)CN (50)	343
"	1-C ₁₀ H ₇ CH(C ₂ H ₅ - <i>i</i>)CN (93)	728,729
"	1-C ₁₀ H ₇ C(C ₂ H ₅ - <i>i</i>) ₂ CN (94)	732,729
"	1-C ₁₀ H ₇ CH[(CH ₂) ₂ N(CH ₂) ₂]CN (82)	741
C ₆ H ₆	1-C ₁₀ H ₇ CH[CH(CH ₂)CH ₂ N(CH ₂) ₂]CN (93)	740
"	1-C ₁₀ H ₇ CH[(CH ₂) ₂ N(CH ₂) ₂]CN (88)	740
Et ₂ O	1-C ₁₀ H ₇ CH[CH ₂ (C ₆ H ₅ -O-2)]CN (72)	736
"	1-C ₁₀ H ₇ CH(CN)CH ₂ 	736

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₂ (Contd.)	2-Naphthylacetonitrile  C ₆ H ₅ CH(C ₄ H _{9-n})CN	2-(Chloromethyl)thiophene ^f <i>i</i> -C ₃ H ₇ Br  (C ₂ H ₅ O) ₂ CHCH ₂ Br (C ₂ H ₅) ₂ N(CH ₂) ₂ Cl BrCH ₂ CO ₂ C ₄ H _{9-r} C ₂ H ₅ CHBrCO ₂ C ₂ H ₅	NaNH ₂ " " " LiNH ₂ 50% aq NaOH. [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂
	C ₆ H ₅ CH(C ₄ H _{9-sec})CN 	4-(2-Chloroethyl)morpholine <i>n</i> -C ₆ H ₁₃ Br (<i>Z</i>)-1-Iodo-3-hexene	" K, AlO ₃ LDA
	 1-Naphthylacetonitrile	 <i>n</i> -C ₆ H ₁₃ Br ^f C ₆ H ₁₁ Br (C ₂ H ₅) ₂ N(CH ₂) ₂ Cl " HO ₂ C-  -CH ₂ Cl ^f  1-(2-Chloroethyl)pyrrolidine ^f 4-(2-Chloroethyl)morpholine " "  " " " C ₆ H ₁₁ Br ^f	LiN(C ₂ H ₅) ₂ NaNH ₂ " " 50% aq NaOH. [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl ^f NaH NaNH ₂ " " " " " C ₆ H ₁₁ Br ^f
	3-CH ₃ OC ₆ H ₄ CH(C ₃ H _{7-n})CN C ₆ H ₅ CH(C ₄ H _{9-n})CN	<i>n</i> -C ₇ H ₁₅ CHBrCO ₂ C ₂ H ₅ C ₆ H ₅ CH ₂ Cl "	NaNH ₂ 50% aq NaOH. [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

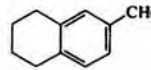

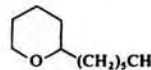
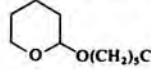
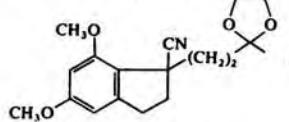
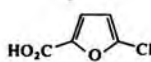



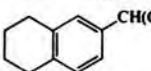
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
"	1-C ₁₀ H ₇ CH[CH ₂ (C ₄ H ₉ S-2)]CN (72)	664,742,743
C ₆ H ₆	2-C ₁₀ H ₇ CH(C ₃ H ₇₋₁)CN (78)	729
Et ₂ O or C ₆ H ₆	 (38)	727
Et ₂ O	C ₆ H ₅ C(C ₄ H _{9-n})[CH ₂ CH(OC ₂ H ₅) ₂]CN (80-82)	637,638
"	C ₆ H ₅ C(C ₄ H _{9-n})[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN (44)	662
Toluene	" (44)	663
"	C ₆ H ₅ C(C ₄ H _{9-n})(CH ₂ CO ₂ C ₄ H _{9-r})CN (69)	78
Et ₂ O	C ₆ H ₅ C(C ₄ H _{9-n})[CH(C ₂ H ₅)CO ₂ C ₂ H ₅]CN (46)	683,685
C ₆ H ₆	C ₆ H ₅ C(C ₃ H _{7-sec})(CN)(CH ₂) ₂ N  (94)	681
THF, -60°	 (48)	553
THF, -78°	 (—)	165
THF, HMPA, -78°	 (91)	744
Et ₂ O	1-C ₁₀ H ₇ CH(C ₆ H _{13-n})CN (86)	728,729
"	1-C ₁₀ H ₇ CH(C ₆ H ₁₁)CN (65)	728,729
"	1-C ₁₀ H ₇ CH[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN (93)	740
"	" (85)	97
C ₆ H ₆	HO ₂ C-  (—)	634
Et ₂ O	1-C ₁₀ H ₇ CH(CN)CH ₂  (76)	664,742
"	1-C ₁₀ H ₇ CH[(CH ₂) ₂ N(CH ₂) ₆]CN (75)	664,745
C ₆ H ₆	1-C ₁₀ H ₇ CH(CN)(CH ₂) ₂ N  (93)	740
"	1-C ₁₀ H ₇ C(CN)[(CH ₂) ₂ N ] (—)	740
	1-C ₁₀ H ₇ CH(CH ₂ Ar)CN I	
Et ₂ O	I Ar = C ₂ H ₄ N-2 (64)	664,743,746
"	I Ar = C ₂ H ₄ N-3 (47)	664,743,745
"	I Ar = C ₂ H ₄ N-4 (64)	664,743
C ₆ H ₆ or Et ₂ O	 (49)	727
C ₆ H ₆	3-CH ₃ OC ₆ H ₄ C(C ₃ H _{7-n})[CH(C ₃ H _{7-n})CO ₂ C ₂ H ₅]CN (23)	720
"	C ₆ H ₅ C(C ₄ H _{9-n})(CH ₂ C ₆ H ₅)CN (44)	68
NH ₃ , Et ₂ O	" (82.91% pure)	162

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₂ (Cont'd.)	C ₆ H ₅ CH(C ₄ H _{9-n})CN	<i>N</i> -(3-Bromopropyl)succinimide	NaNH ₂
		(C ₂ H ₅ O) ₂ CHCH(CH ₃)Br	"
		<i>n</i> -C ₇ H ₁₅ CHBrCO ₂ C ₂ H ₅	"
	C ₆ H ₅ CH(C ₄ H _{9-sec})CN	C ₆ H ₅ CH ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	C ₆ H ₅ CH(C ₄ H ₉₋₇)CN	"	NaNH ₂
		"	"
	Cyanomethylferrocene	"	<i>n</i> -C ₄ H ₉ Li
	1-Naphthylacetonitrile	<i>n</i> -C ₇ H ₁₅ Br ^f	NaNH ₂
		C ₆ H ₅ CH ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	NaH
		C ₆ H ₅ CH ₂ Br	NaNH ₂
		C ₆ H ₅ CH ₂ OH ^f	Na, CH ₃ CO ₂ CH ₂ C ₆ H ₅
			NaNH ₂
		(C ₂ H ₅) ₂ N(CH ₂) ₃ Cl	"
		1-(3-Chloropropyl)pyrrolidine	"
	1-(2-Chloroethyl)piperidine ^f	"	
	4-(3-Chloropropyl)morpholine	"	
2-Naphthylacetonitrile	<i>n</i> -C ₇ H ₁₅ Br ^f	"	
	C ₆ H ₅ CH ₂ Cl	"	
	C ₆ H ₅ CH ₂ OH ^f	Na, CH ₃ CO ₂ CH ₂ C ₆ H ₅	
	C ₆ H ₅ CH ₂ Cl ^f	NaNH ₂	
C ₆ H ₅ CH(C ₄ H _{9-n})CN	(C ₂ H ₅ O) ₂ CHCH(C ₂ H ₅)Br	"	
	<i>n</i> -C ₄ H ₉ CHBrCO ₂ C ₂ H ₅	"	
1-Naphthylacetonitrile	<i>n</i> -C ₈ H ₁₇ Br ^f	"	
	<i>n</i> -C ₈ H ₁₇ OH ^f	Na, CH ₃ CO ₂ C ₆ H _{11-n}	
	2-CH ₃ OC ₆ H ₄ CH ₂ Cl	Na, C ₆ H ₅ CO ₂ CH ₃	
	C ₆ H ₅ (CH ₂) ₂ Br ^f	NaH	
	"	NaNH ₂	
	1-(3-Chloropropyl)piperidine	"	
	1,4-Bis(2-chloroethyl)piperazine	"	
2-Naphthylacetonitrile	<i>n</i> -C ₈ H ₁₇ OH ^f	Na, CH ₃ CO ₂ C ₆ H _{11-n}	
		NaNH ₂	
C ₆ H ₅ CH(C ₄ H _{9-n})CN	(C ₂ H ₅ O) ₂ CHCH(C ₂ H ₅ - <i>n</i>)Br	"	
	C ₆ H ₅ CO ₂ (CH ₂) ₂ Br	"	
1-Naphthylacetonitrile		NaH	
C ₆ H ₅ CH(C ₄ H _{9-n})CN	(C ₂ H ₅ O) ₂ CHCH(C ₄ H _{9-n})Br	"	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

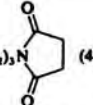
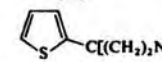


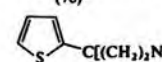

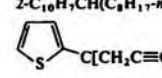
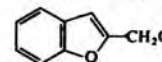
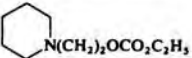
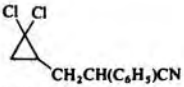
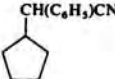

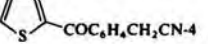
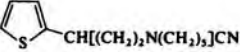
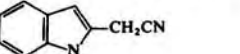
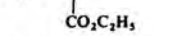

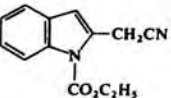
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ H ₆ , DMF	 (48)	643
Et ₂ O	C ₆ H ₅ C(C ₄ H _{9-n})[CH(CH ₃)CH(OC ₂ H ₅) ₂]CN (50)	685,689
"	C ₆ H ₅ C(C ₄ H _{9-n})[CH(C ₂ H ₅ - <i>n</i>)CO ₂ C ₂ H ₅]CN (50)	683,685
"	C ₆ H ₅ C(C ₄ H _{9-sec})(CH ₂ C ₆ H ₅)CN (-)	68
"	C ₆ H ₅ C(C ₄ H ₉₋₇)(CH ₂ C ₆ H ₅)CN (41)	68
C ₆ H ₆	" (48)	343
"	 (53)	567
Et ₂ O	FcC(CH ₂ C ₆ H ₅) ₂ CN (70), FcC(CH ₂ C ₆ H ₅)[C(NH)CH ₂ Fc]CN (5)	49
"	1-C ₁₀ H ₇ CH(C ₇ H _{15-n})CN (88)	728,729
"	1-C ₁₀ H ₇ CH(CH ₂ C ₆ H ₅)CN (95)	97
"	1-C ₁₀ H ₇ C(CH ₂ C ₆ H ₅) ₂ CN (78)	97
C ₆ H ₆	1-C ₁₀ H ₇ CH(CH ₂ C ₆ H ₅)CN (-)	634
Toluene	" (81)	747
Et ₂ O	" (96)	728-730
"	" (64) ^f	309,311,311
Et ₂ O	1-C ₁₀ H ₇ CH(CN)(CH ₂) ₃  (69)	736
C ₆ H ₆	1-C ₁₀ H ₇ CH[(CH ₂) ₃ N(C ₂ H ₅) ₂]CN (74)	741
"	1-C ₁₀ H ₇ CH[(CH ₂) ₃ N(CH ₂) ₆]CN (61)	741
Et ₂ O	1-C ₁₀ H ₇ CH[(CH ₂) ₂ N(CH ₂) ₂]CN (77)	664,745,740, 743
C ₆ H ₆	1-C ₁₀ H ₇ CH(CN)(CH ₂) ₃  (92)	741
"	2-C ₁₀ H ₇ CH(C ₇ H _{15-n})CN (74)	729
Toluene	2-C ₁₀ H ₇ CH(CH ₂ C ₆ H ₅)CN (-)	747
"	" (76) ^f	309,313,311
"	 (68)	567
Et ₂ O	C ₆ H ₅ C(C ₄ H _{9-n})[CH(C ₂ H ₅)CH(OC ₂ H ₅) ₂]CN (43)	689,685
"	C ₆ H ₅ C(C ₄ H _{9-n})[CH(C ₂ H ₅ - <i>n</i>)CO ₂ C ₂ H ₅]CN (56)	683,685
"	1-C ₁₀ H ₇ CH(C ₈ H _{17-n})CN (84)	728,729
"	" (67) ^f	314
"	" (67) ^f	312
DMF	1-C ₁₀ H ₇ CH(CH ₂ C ₆ H ₅ OCH ₂) ₂ CN (-)	634
Et ₂ O	1-C ₁₀ H ₇ CH[(CH ₂) ₂ C ₆ H ₅]CN (90)	728
Toluene	" (62)	747
C ₆ H ₆	1-C ₁₀ H ₇ CH[(CH ₂) ₃ N(CH ₂) ₂]CN (89)	741
Et ₂ O	1-C ₁₀ H ₇ CH(CN)(CH ₂) ₃  N(CH ₂) ₂ CH(CN)C ₁₀ H ₇₋₁ (-)	740
"	2-C ₁₀ H ₇ CH(C ₈ H _{17-n})CN (85) ^f	314
"	 (74)	567
Et ₂ O	C ₆ H ₅ C(C ₄ H _{9-n})[CH(C ₂ H ₅ - <i>n</i>)CH(OC ₂ H ₅) ₂]CN (48)	689,685
C ₆ H ₆ , DMF	C ₆ H ₅ C(C ₄ H _{9-n})[(CH ₂) ₂ OCOC ₆ H ₅]CN (40)	714,715
DMF	 (-)	634
Et ₂ O	C ₆ H ₅ C(C ₄ H _{9-n})[CH(C ₄ H _{9-n})CH(OC ₂ H ₅) ₂]CN (45)	689,685

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₂ (Contd.)	C ₆ H ₅ CH(C ₄ H ₉ - <i>sec</i>)CN		CH ₃ CO ₂ K
	1-Naphthylacetonitrile	<i>n</i> -C ₁₀ H ₂₁ Br CH ₂ =CH(CH ₂) ₈ Cl 2,6-(CH ₃) ₂ C ₆ H ₃ O(CH ₂) ₂ Cl ^f (CH ₂) ₂ NCH ₂ CH(C ₆ H ₅)Cl C ₆ H ₅ CH ₂ N(CH ₂)(CH ₂) ₂ Cl	" NaNH ₂ NaH NaNH ₂ "
	C ₆ H ₅ CH(C ₄ H ₉ - <i>n</i>)CN	<i>N</i> -(3-Bromopropyl)phthalimide	"
	1-Naphthylacetonitrile	6-(Chloromethyl)tetralin CH ₂ =CH(CH ₂) ₉ Cl <i>n</i> -C ₁₂ H ₂₅ Br ^f [(CH ₂) ₂ C=CHCH ₂] ₂ N(CH ₂) ₂ Cl	" " " "
		1-Chloroacenaphthene	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
C ₁₃		(C ₆ H ₅) ₂ CHCl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	1-Naphthylacetonitrile	(<i>Z</i>)- <i>n</i> -C ₈ H ₁₇ CH=CH(CH ₂) ₈ Cl ^f	NaNH ₂
	(C ₂ H ₅) ₂ CHCH(C ₆ H ₅)CN	CH ₃ I	NaH
		"	NaNH ₂
		"	"
		"	NaH
		CH ₃ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		CH ₃ I ^f	NaNH ₂
		CH ₃ I	LDA
	<i>n</i> -C ₄ H ₉ C(C ₂ H ₅ - <i>n</i>) ₂ CH ₂ CN	C ₂ H ₅ Br	NaNH ₂
	3-CH ₃ OC ₆ H ₄ CH(C ₄ H ₉ - <i>n</i>)CN 3,4-(CH ₃) ₂ C ₆ H ₃ CH(C ₂ H ₅ - <i>n</i>)CN	Cl(CH ₂) ₂ Cl 	" "
	(1-C ₁₀ H ₇)CH(CH ₃)CN	C ₂ H ₅ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	C ₂ H ₅ I	LDA	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

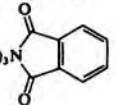
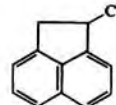
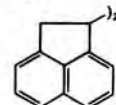
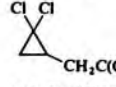

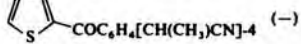
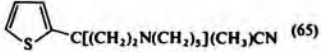
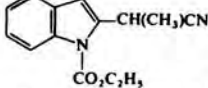
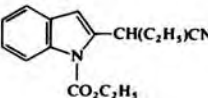
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	C ₆ H ₅ C(C ₄ H ₉ - <i>sec</i>)[(CH ₂) ₂ N(CH ₂) ₂]CN (—)	748
Toluene	1-C ₁₀ H ₇ CH(C ₁₀ H ₂₁ - <i>n</i>)CN (64)	747
—	1-C ₁₀ H ₇ CH[(CH ₂) ₈ CH=CH ₂]CN (—)	743
DMF	2,6-(CH ₃) ₂ C ₆ H ₃ O(CH ₂) ₂ CH(C ₁₀ H ₇ -1)CN (—)	634
C ₆ H ₆	1-C ₁₀ H ₇ CH[CH(C ₆ H ₅)CH ₂ N(CH ₂) ₂]CN (83)	740
"	1-C ₁₀ H ₇ CH[(CH ₂) ₂ N(CH ₂)CH ₂ C ₆ H ₅]CN (80)	740
C ₆ H ₆ , DMF	 (56)	643
Et ₂ O	C ₆ H ₅ C(C ₄ H ₉ - <i>n</i>)(CH ₂ C ₁₀ H ₁₁)CN (35)	343
"	1-C ₁₀ H ₇ CH[(CH ₂) ₈ CH=CH ₂]CN (80)	664
"	1-C ₁₀ H ₇ CH(C ₁₂ H ₂₅ - <i>n</i>)CN (79)	728,729
C ₆ H ₆	1-C ₁₀ H ₇ CH[(CH ₂) ₂ N(CH ₂ CH=C(CH ₃) ₂) ₂]CN (—)	749
—	 (58),  (7)	81
—	 (50)	79
Et ₂ O	1-C ₁₀ H ₇ CH[(CH ₂) ₈ CH=CHC ₆ H ₁₇ - <i>n</i>]CN (62)	664
—	(C ₂ H ₅) ₂ CHC(C ₆ H ₅)(CH ₃)CN (66)	692
Xylene	C ₆ H ₅ C(C ₂ H ₉)(CH ₃)CN (—)	631
—	 (80)	731
HMPA	 (—)	750
—	" (—)	750
—	 (65)	567
THF, -78°	 (90)	751
Et ₂ O	<i>n</i> -C ₄ H ₉ C(C ₂ H ₅ - <i>n</i>) ₂ CH(C ₂ H ₅)CN I, <i>n</i> -C ₄ H ₉ C(C ₂ H ₅ - <i>n</i>) ₂ C(C ₂ H ₅)=C=NC ₂ H ₅ II, (89, ratio of I:II = 97:3)	256
C ₆ H ₆	3-CH ₃ OC ₆ H ₄ C(C ₄ H ₉ - <i>n</i>)[(CH ₂) ₂ Cl]CN (56)	720
Et ₂ O	3,4-(CH ₃) ₂ C ₆ H ₃ C(C ₂ H ₅ - <i>n</i>)[(CH ₂) ₂ OH]CN (—)	673,674
"	1-C ₁₀ H ₇ C(CH ₃)(C ₂ H ₅)CN (88)	729
"	" (61)	97
THF, -78°	 (55)	751

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₃ (Contd.)	C ₆ H ₅ CH[(CH ₂) ₂ N(CH ₃) ₂]CN (C ₂ H ₅) ₂ CHCH(C ₆ H ₅)CN C ₆ H ₅ CH(C ₂ H _{11-n})CN 3,4-(CH ₂ O) ₂ C ₆ H ₃ CH(C ₂ H _{7-i})CN	<i>i</i> -C ₃ H ₇ Br " Cl(CH ₂) ₂ Br <i>i</i> -C ₃ H ₇ Br ^c	NaNH ₂ NaH NaNH ₂ "
	 CH[(CH ₂) ₂ N(CH ₃) ₂]CN	CH ₂ =CHCH ₂ Br ^c	"
	<i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ CH ₂ CN	<i>n</i> -C ₄ H ₉ Br	"
		<i>i</i> -C ₄ H ₉ Br	"
		<i>i</i> -C ₄ H ₉ Cl <i>sec</i> -C ₄ H ₉ Br	" "
	3,4-(CH ₂ O) ₂ C ₆ H ₃ CH(C ₂ H _{7-i})CN	CH ₂ N(CHO)(CH ₂) ₂ Cl	"
	 CH(C ₆ H ₅)CN	BrCH ₂ CO ₂ C ₂ H ₅	"
	2-(1-Naphthyl)propionitrile	(CH ₃) ₂ N(CH ₂) ₂ Cl	"
	 CH ₂ CH(C ₆ H ₅)CN	"	"
	 CH ₂ CH(C ₆ H ₄ X-4)CN	"	KNH ₂
 CH(C ₆ H ₅)CN	"	"	
(2-C ₂ H ₄ N)CH(C ₆ H ₅)CN	"	NaNH ₂ LiNH ₂	
<i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ CH ₂ CN	<i>i</i> -C ₃ H ₇ Br	NaNH ₂	
3,4-(CH ₂ O) ₂ C ₆ H ₃ CH(C ₂ H _{7-i})CN	CH ₂ N(CHO)(CH ₂) ₂ Cl ^c	"	
2-(1-Naphthyl)propionitrile	(CH ₃) ₂ NCH ₂ CH(CH ₃)Cl 2-(Chloromethyl)furan	NaNH ₂ NaH	
 CH ₂ CH(C ₆ H ₅)CN	(CH ₃) ₂ N(CH ₂) ₂ Cl	KNH ₂	
<i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ CH ₂ CN	C ₆ H ₁₁ Br	"	
C ₆ H ₅ CH(C ₂ H _{11-n})CN	BrCH ₂ CO ₂ C ₄ H _{9-i} (C ₂ H ₅ O) ₂ CHCH ₂ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂	
 CH(C ₆ H ₅)CN	"	"	
2-(1-Naphthyl)propionitrile	4-(2-Chloroethyl)morpholine	"	
 CH ₂ CH(C ₆ H ₅)CN	R ¹ R ² N(CH ₂) ₂ Cl	KNH ₂	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)








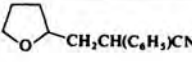
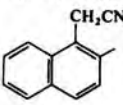
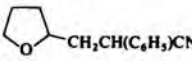
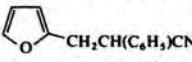
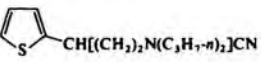
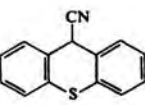
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	C ₆ H ₅ C(CN)(C ₂ H _{7-i})[(CH ₂) ₂ N(CH ₃) ₂]CN (—)	629
—	(C ₂ H ₅) ₂ CHC(C ₆ H ₅)(C ₂ H _{7-i})CN (57)	692
C ₆ H ₆	C ₆ H ₅ C(C ₂ H _{11-n})[(CH ₂) ₂ N(CH ₃) ₂]CN (—)	721
DME	3,4-(CH ₂ O) ₂ C ₆ H ₃ C(C ₂ H _{7-i}) ₂ CN (80)	699
—	 Cl[(CH ₂) ₂ N(CH ₃) ₂](CH ₂ CH=CH ₂)CN (81)	567
Various solvents	<i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ CH(C ₆ H _{9-n})CN (78-100), <i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ C(C ₆ H _{9-n})=C=NC ₆ H _{9-n} (2-22), <i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ C(C ₆ H _{9-n}) ₂ CN (0-20)	256
Et ₂ O	<i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ CH(C ₆ H _{9-i})CN I, <i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ C(C ₆ H _{9-i})=C=NC ₆ H _{9-i} II, (75, I:II = 88:12)	256
"	I, II (38, I:II = 86:14)	256
"	<i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ CH(C ₆ H _{9-sec})CN I, <i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ C(C ₆ H _{9-sec})=C=NC ₆ H _{9-sec} II, (30, I:II = 80:20)	256
Toluene	3,4-(CH ₂ O) ₂ C ₆ H ₃ C(C ₂ H _{7-i})[(CH ₂) ₂ N(CH ₃) ₂]CHO]CN (—)	699
C ₆ H ₆ , DMF	C ₆ H ₅ C(C ₂ H ₉)(CH ₂ CO ₂ C ₂ H ₅)CN (60)	630,752
C ₆ H ₆	1-C ₁₀ H ₇ C(CH ₃)[(CH ₂) ₂ N(CH ₃) ₂]CN (80)	740
"	 CH ₂ C(C ₆ H ₅)[(CH ₂) ₂ N(CH ₃) ₂]CN (52)	753
Toluene	 CH ₂ C(C ₆ H ₄ X-4)[(CH ₂) ₂ N(CH ₃) ₂]CN I I, X = H (—) I, X = Cl (—)	635,753
"	 C(C ₆ H ₅)[(CH ₂) ₂ N(CH ₃) ₂]CN (54)	753
—	(2-C ₂ H ₄ N)C(C ₆ H ₅)[(CH ₂) ₂ N(CH ₃) ₂]CN (81)	662
Toluene	" (81)	663
Et ₂ O	<i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ CH(C ₂ H _{11-i})CN I, <i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ C(C ₂ H _{11-i})=C=NC ₂ H _{11-i} II, (73, I:II = 93:7)	256
Toluene, or DME, or xylene, or dioxane	3,4-(CH ₂ O) ₂ C ₆ H ₃ C(C ₂ H _{7-i})[(CH ₂) ₂ N(CHO)CH ₃]CN (58)	699
C ₆ H ₆	1-C ₁₀ H ₇ C(CH ₃)[CH(CH ₃)CH ₂ N(CH ₃) ₂]CN (72)	740
DMF	(2-C ₂ H ₅ O)CH ₂ C(CH ₃)(C ₁₀ H ₇₋₁)CN (86)	634
Toluene	 CH ₂ C(C ₆ H ₅)[(CH ₂) ₂ N(CH ₃) ₂]CN (—)	635,753
Et ₂ O	<i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ CH(C ₆ H ₁₁)CN I, <i>n</i> -C ₄ H ₉ C(C ₂ H _{7-n}) ₂ C(C ₆ H ₁₁)=C=NC ₆ H ₁₁ II, (55, I:II = 87:13)	256
—	C ₆ H ₅ C(C ₂ H _{11-n})(CH ₂ CO ₂ C ₄ H _{9-i})CN (—)	78
Et ₂ O	C ₆ H ₅ C(C ₂ H _{11-n})[CH ₂ CH(OC ₂ H ₅) ₂]CN (82-85)	637,638
C ₆ H ₆	C ₆ H ₅ C(C ₂ H ₉)[CH ₂ CH(OC ₂ H ₅) ₂]CN (75)	630,752
—	1-C ₁₀ H ₇ C(CH ₃)(CN)(CH ₂) ₂ N  (—)	740
Toluene	 CH ₂ C(C ₆ H ₅)[(CH ₂) ₂ NR ¹ R ²]CN I I, R ¹ = R ² = C ₂ H ₅ (—) I, R ¹ , R ² = (CH ₂) ₄ (—) I, R ¹ , R ² = (CH ₂) ₂ O(CH ₂) ₂ (—)	635,753

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₃ (Contd.)		(C ₂ H ₅) ₂ N(CH ₂) ₂ Cl	"
		4-(2-Chloroethyl)morpholine	"
	(2-C ₂ H ₅ N)CH(C ₆ H ₅)CN	(C ₂ H ₅) ₂ N(CH ₂) ₂ Cl	NaNH ₂
	<i>n</i> -C ₄ H ₉ C(C ₂ H ₅ - <i>n</i>) ₂ CH ₂ CN	C ₆ H ₅ CH ₂ Cl	LiNH ₂
	C ₆ H ₅ CH(C ₂ H ₅ - <i>n</i>)CN	"	NaNH ₂
	C ₆ H ₅ CH(C ₂ H ₅ - <i>i</i>)CN	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
	2-(1-Naphthyl)propionitrile	1-(2-Chloroethyl)piperidine	NaNH ₂
		C ₆ H ₅ CH ₂ Cl	"
		1-(2-Chloroethyl)piperidine	KNH ₂
		"	"
	<i>n</i> -C ₄ H ₉ C(C ₂ H ₅ - <i>n</i>) ₂ CH ₂ CN	<i>n</i> -C ₈ H ₁₇ Br	NaNH ₂
	C ₆ H ₅ CH[(CH ₂) ₃ CH=CH ₂]CN	4-O ₂ NC ₆ H ₄ CH ₂ Cl	NaOH
	C ₆ H ₅ CH(C ₂ H ₅ - <i>n</i>)CN	BrCH ₂ CO ₂ C ₆ H ₁₁	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
	2-(1-Naphthyl)propionitrile	1,4-Bis(2-chloroethyl)piperazine	NaNH ₂
	3-(2-Furyl)-2-phenylpropionitrile	1-(2-Chloroethyl)-2-methylpiperidine	KNH ₂
	2-(1-Naphthyl)propionitrile	(CH ₂) ₂ NCH ₂ CH(C ₆ H ₅)Cl	NaNH ₂
	C ₆ H ₅ CH(C ₂ H ₅ - <i>n</i> -2)CN	(<i>i</i> -C ₂ H ₅) ₂ N(CH ₂) ₂ OCO ₂ C ₂ H ₅	CH ₃ CO ₂ K
	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH(C ₂ H ₅ - <i>i</i>)CN	4-ClC ₆ H ₄ (CH ₂) ₂ N(CH ₃)(CH ₂) ₂ Cl	NaNH ₂
		3,4-(CH ₃ O) ₂ C ₆ H ₃ (CH ₂) ₂ N(CH ₃)(CH ₂) ₂ Cl	"
			"
			"
			"
C ₁₄	C ₆ H ₅ CH(C ₆ H ₁₁)CN	CH ₃ I	"
	4-(C ₆ H ₅)C ₆ H ₄ CH ₂ CN	"	"
		CH ₃ I'	"
	(C ₆ H ₅) ₂ CHCN	CH ₃ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
		CH ₃ Br ₂	NaNH ₂
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
		CH ₂ Cl ₂	"
	9-Cyanofluorene	CH ₃ I	NaOCH ₃
		"	"
		"	"
		CH ₂ Br ₂	<i>i</i> -C ₄ H ₉ OK
		CH ₃ I	CH ₃ MgI
	C ₆ H ₅ CH[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN	C ₂ H ₅ Br'	70% aq NaOH

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

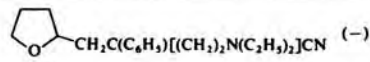
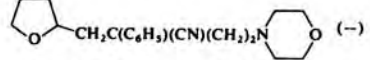
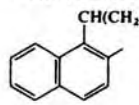
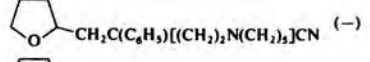
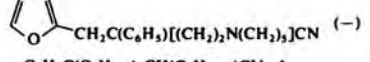
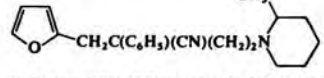
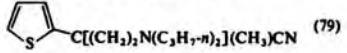
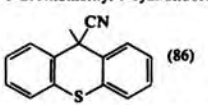



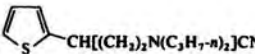

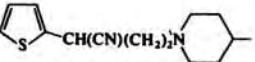
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
"	 (-)	753
"	 (-)	753
—	(2-C ₂ H ₅ N)C(C ₆ H ₅)[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN (78)	662
Toluene	" (78)	663
—	C ₆ H ₅ C(C ₂ H ₅ - <i>n</i>)(CH ₂ C ₆ H ₅)CN (31)	256
—	C ₆ H ₅ C(C ₂ H ₅ - <i>n</i>)(CH ₂ C ₆ H ₅)CN (31)	68
—	C ₆ H ₅ C(C ₂ H ₅ - <i>i</i>)(CH ₂ C ₆ H ₅)CN (31)	68
C ₆ H ₆	1-C ₁₀ H ₇ C(CH ₃)[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN (73)	740
Toluene	 (-)	747
"	 (-)	753
—	 (-)	753,63
Et ₂ O	<i>n</i> -C ₄ H ₉ C(C ₂ H ₅ - <i>n</i>) ₂ CH(C ₆ H ₁₁ - <i>n</i>)CN I, <i>n</i> -C ₄ H ₉ C(C ₂ H ₅ - <i>n</i>) ₂ C(C ₆ H ₁₁ - <i>n</i>)=C=NC ₆ H ₁₁ - <i>n</i> II (93, I:II = 92:8)	256
DMF	C ₆ H ₅ C[(CH ₂) ₃ CH=CH ₂](CH ₂ C ₆ H ₄ NO ₂ -4)CN (80)	754
C ₆ H ₆	" (40)	754
—	C ₆ H ₅ C(C ₂ H ₅ - <i>n</i>)(CH ₂ CO ₂ C ₆ H ₁₁)CN (26)	78
C ₆ H ₆	1-C ₁₀ H ₇ C(CH ₃)(CN)(CH ₂) ₂ N(CH ₂) ₂ C(CH ₃)(CN)C ₁₀ H ₇ -1 (-)	740
Toluene		753
C ₆ H ₆	(1-C ₁₀ H ₇)C(CH ₃)[CH(C ₆ H ₅)CH ₂ N(CH ₃) ₂]CN (68)	740
—	C ₆ H ₅ C(C ₂ H ₅ - <i>n</i> -2)[(CH ₂) ₂ N(C ₂ H ₅ - <i>i</i>) ₂]CN (-)	748
Toluene	3,4-(CH ₃ O) ₂ C ₆ H ₃ C(C ₂ H ₅ - <i>i</i>)[(CH ₂) ₂ N(CH ₃)(CH ₂) ₂ C ₆ H ₄ Cl-4]CN (74)	717
—	3,4-(CH ₃ O) ₂ C ₆ H ₃ C(C ₂ H ₅ - <i>i</i>)[(CH ₂) ₂ N(CH ₃)(CH ₂) ₂ C ₆ H ₃ (OCH ₃) ₂ -3,4]CN I'	717
—	I, <i>n</i> = 2 (71)	717
—	I, <i>n</i> = 3 (77)	717
Xylene	C ₆ H ₅ C(C ₆ H ₁₁)(CH ₂)CN (70)	631
Et ₂ O	4-(C ₆ H ₅)C ₆ H ₄ CH(CH ₃)CN (63)	755
C ₆ H ₆	4-(C ₆ H ₅)C ₆ H ₄ C(CH ₃) ₂ CN (68)	604
—	 (79)	567
—	(C ₆ H ₅) ₂ C(CH ₃)CN (-)	67
—	[(C ₆ H ₅) ₂ C(CN)] ₂ CH ₂ (-)	756
—	(C ₆ H ₅) ₂ C(CH ₂ Br)CN (93)	693
—	(C ₆ H ₅) ₂ C(CH ₂ Cl)CN (82)	693
CH ₃ OH	9-Cyano-9-methylfluorene (56)	757
—	" (ca. 95)	138
—	" (-)	758
<i>i</i> -C ₄ H ₉ OH	9-Bromomethyl-9-cyanofluorene (68)	757
Et ₂ O	 (86)	52
—	C ₆ H ₅ C[(CH ₂) ₂ N(C ₂ H ₅) ₂](C ₂ H ₅)CN (84)	76

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₄ (Contd.)	4-C ₆ H ₅ C ₆ H ₄ CH ₂ CN	C ₂ H ₅ Br	NaNH ₂
	4-C ₆ H ₁₁ C ₆ H ₄ CH ₂ CN	"	"
	4-C ₆ H ₅ OC ₆ H ₄ CH ₂ CN	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(CH ₃) ₂]Cl
	(C ₆ H ₅) ₂ CHCN	"	NaNH ₂
	"	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	"	"	C ₁₀ H ₈ Na
	"	Cl(CH ₂) ₂ Cl	NaNH ₂
	"	Br(CH ₂) ₂ Br	50% aq NaOH, dibenzo[18]-crown-6
	"	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	"	"	NaNH ₂
	"	"	"
	"	ClCH ₂ OCH ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	"	CH ₃ OCH ₂ Cl	"
	"	ClCH ₂ CN	"
			
	C ₆ H ₅ CH(CN)(CH ₂) ₂ N 	C ₂ H ₅ Br	"
		C ₂ H ₅ Br ^r	C ₂ H ₅ Br
	9-Cyanofluorene	C ₂ H ₅ I	NaOCH ₃
		Cl(CH ₂) ₂ Cl	NaNH ₂
	C ₆ H ₅ CH(C ₆ H ₁₁)CN	Cl(CH ₂) ₂ Br	"
	4-C ₆ H ₅ OC ₆ H ₄ CH ₂ CN	CH ₂ =CHCH ₂ Br ^r	"
	4-C ₆ H ₅ C ₆ H ₄ CH ₂ CN	n-C ₃ H ₇ Br	"
	"	n-C ₃ H ₇ I	"
	"	"	"
	(C ₆ H ₅) ₂ CHCN	CH ₂ =CHCH ₂ Br ^r	"
	"	n-C ₃ H ₇ Br	"
	"	n-C ₃ H ₇ I	t-C ₄ H ₉ OK
	"	CH ₂ =CHCH ₂ Br	NaH
	"	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	"	HC≡CCH ₂ Cl	LiNH ₂
	"	HC≡CCH ₂ Br	NaNH ₂
	"	CH ₃ CHClCH ₂ Cl	"
	"	Br(CH ₂) ₂ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	"	"	50% aq NaOH, [CH ₂ =CHCH ₂ N(C ₂ H ₅) ₂]Cl
	"	"	NaNH ₂
	"	"	"
	"	Cl(CH ₂) ₂ Br	50% aq NaOH
	"	"	NaNH ₂
	"	"	"
	"	Cl(CH ₂) ₂ CN	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	"	CH ₃ OCH(CH ₂)Cl	"
	"	CH ₃ S(CH ₂) ₂ Cl	NaNH ₂
	"	Cl ₂ CHCO ₂ CH ₃	NaOCH ₃
	"		t-C ₄ H ₉ OK
		RX ^r	NaNH ₂

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

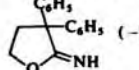


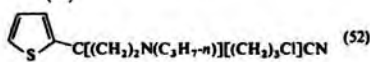
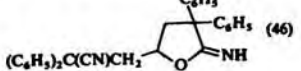
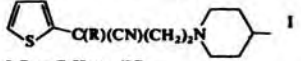
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ H ₆	4-C ₆ H ₅ C ₆ H ₄ C(C ₂ H ₅) ₂ CN (80)	755,604
Et ₂ O	" (86)	759
—	4-C ₆ H ₁₁ C ₆ H ₄ CH(C ₂ H ₅)CN (81)	760
—	4-C ₆ H ₅ OC ₆ H ₄ CH(C ₂ H ₅)CN (82)	761
—	(C ₆ H ₅) ₂ C(C ₂ H ₅)CN (92)	67
THF	" (77)	198
—	(C ₆ H ₅) ₂ C[(CH ₂) ₂ Cl]CN (83)	702
—	(C ₆ H ₅) ₂ C[(CH ₂) ₂ Br]CN (75)	527
—	" (91)	693-695,85
C ₆ H ₆	" (-)	762
—	[(C ₆ H ₅) ₂ C(CN)CH ₂] ₂ (5)	763,756
—	[(C ₆ H ₅) ₂ C(CN)CH ₂] ₂ O (90)	72
—	(C ₆ H ₅) ₂ C(CH ₂ OCH ₃)CN (80)	72
—	(C ₆ H ₅) ₂ C(CH ₂ CN)CN (93)	73
NH ₃	 (-)	179
C ₆ H ₆	C ₆ H ₅ C(C ₂ H ₅)(CN)(CH ₂) ₂ N  (88)	681
—	 (48)	567
CH ₃ OH	9-Cyano-9-ethylfluorene (ca. 95)	138
—	" (-)	764,758
—	 (52)	567
C ₆ H ₆	C ₆ H ₅ C(C ₆ H ₁₁)[(CH ₂) ₂ Cl]CN (-)	721
Et ₂ O	4-C ₆ H ₅ OC ₆ H ₄ CH(CH ₂ CH=CH ₂)CN (75)	761
C ₆ H ₆	4-C ₆ H ₅ C ₆ H ₄ CC(C ₂ H ₅) ₂ CN (78)	604
Et ₂ O	4-C ₆ H ₅ C ₆ H ₄ CH(C ₂ H ₅)CN (72)	755
"	" (-)	765
"	4-C ₆ H ₅ C ₆ H ₄ CH(CH ₂ CH=CH ₂)CN (85)	755
—	(C ₆ H ₅) ₂ C(C ₂ H ₅)CN (-)	766
—	" (-)	767
—	(C ₆ H ₅) ₂ C(CH ₂ CH=CH ₂)CN (72)	768
—	" (95)	67
NH ₃	(C ₆ H ₅) ₂ C(CH ₂ C≡CH)CN (88)	573
Et ₂ O, C ₆ H ₆	" (60-88)	613
C ₆ H ₆	(C ₆ H ₅) ₂ C(CH ₂ CHClCH ₂)CN (-)	762
—	(C ₆ H ₅) ₂ C[(CH ₂) ₂ Br]CN I (87), ((C ₆ H ₅) ₂ C(CN)CH ₂) ₂ CH ₂ II (67)	693-695
—	II (65)	582
—	II (52)	769-771, 756,763
C ₆ H ₆	I (-)	771
Dioxane	(C ₆ H ₅) ₂ C[(CH ₂) ₂ Cl]CN (94)	772
DMSO	" (79)	701,700
C ₆ H ₆	" (97)	771,614,702
—	(C ₆ H ₅) ₂ CH[(CH ₂) ₂ CN]CN (90)	73
—	(C ₆ H ₅) ₂ C[CH(CH ₃)OCH ₃]CN (50)	72
—	(C ₆ H ₅) ₂ C[(CH ₂) ₂ SCH ₃]CN (42)	211
—	(C ₆ H ₅) ₂ C[CHClCO ₂ CH ₃]CN (-)	773
t-C ₄ H ₉ OH	 (46)	774
—	 I	567
—	I, R = C ₂ H ₅ -t (85)	
—	I, R = CH ₂ CH=CH ₂ (64)	

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₄ (Contd.)	9-Cyanofluorene	<i>n</i> -C ₃ H ₇ I <i>i</i> -C ₃ H ₇ I or Br CH ₂ =CHCH ₂ Br ^f	— NaOCH ₃ "
		RX	NaNH ₂
	4-C ₆ H ₅ OC ₆ H ₄ CH ₂ CN 4-C ₆ H ₅ C ₆ H ₄ CH ₂ CN	CH ₃ CH=CHCH ₂ Br ^f "	NaNH ₂ "
	C ₆ H ₅ CH(CN)(CH ₂) ₂ N(C ₂ H ₅) ₂ C ₆ H ₅ CH(C ₆ H ₁₁)CN	<i>n</i> -C ₄ H ₉ I ^f <i>n</i> -C ₄ H ₉ Br ^f BrCH ₂ CO ₂ C ₂ H ₅ <i>i</i> -C ₄ H ₉ Br (CH ₂) ₂ N(CH ₂) ₂ Cl	70% aq NaOH NaNH ₂ "
	(C ₆ H ₅) ₂ CHCN	<i>n</i> -C ₄ H ₉ Br Cl(CH ₂) ₄ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂
		—	LiNH ₂
		Cl(CH ₂) ₄ Br Br(CH ₂) ₄ Br	LiN(C ₂ H ₅) ₂ 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		—	NaNH ₂
		BrCH ₂ CH(CH ₃)CH ₂ Cl ^f Br(CH ₂) ₂ CH(CH ₃)Br	C ₁₀ H ₈ Na NaNH ₂ "
		<i>i</i> -C ₃ H ₇ OCH ₂ Cl ClCH ₂ CO ₂ C ₂ H ₅ BrCH ₂ CO ₂ C ₂ H ₅	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaH NaNH ₂ "
		Cl ₃ CHCO ₂ C ₂ H ₅ Cl ₃ CCO ₂ C ₂ H ₅ Cl(CH ₂) ₂ CN Br(CH ₂) ₂ CN	NaOC ₂ H ₅ NaOCH ₃ NaNH ₂ 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂
		—	—
		CH ₂ (OC ₂ H ₅) ₂	NaOC ₂ H ₅
	3-Chloro-1-methylazetidene	—	NaNH ₂
	2-(1-Naphthyl)butyronitrile	(CH ₂) ₂ N(CH ₂) ₂ Cl	"
		—	KNH ₂
	(2-C ₃ H ₄ N)CH(CH ₂ C ₆ H ₅)CN 9-Cyanofluorene	—	NaNH ₂
	C ₆ H ₅ CH[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN 4-C ₆ H ₅ C ₆ H ₄ CH ₂ CN	<i>n</i> -C ₄ H ₉ I <i>i</i> -C ₄ H ₉ Br ^f <i>i</i> -C ₃ H ₇ I, Br ^f	NaOCH ₃ 70% aq NaOH NaNH ₂
	4-C ₆ H ₅ OC ₆ H ₄ CH ₂ CN	<i>n</i> -C ₃ H ₇ I, Br ^f "	" "
	2-(Chloromethyl)furan	—	"
	(C ₆ H ₅) ₂ CHCN	<i>n</i> -C ₃ H ₇ I, Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

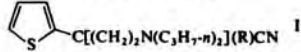
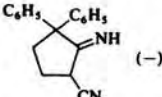
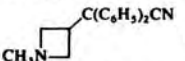
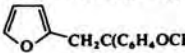

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	9-Cyano-9- <i>n</i> -propylfluorene (—)	758
CH ₃ OH	9-Cyano-9-isopropylfluorene (ca. 95)	138
"	9-Allyl-9-cyanofluorene (69)	757
—	 I	567
	I, R = C ₄ H ₉ - <i>n</i> (74) I, R = (CH ₂) ₄ Cl (38)	
Et ₂ O	4-C ₆ H ₅ OC ₆ H ₄ CH(CH ₂ CH=CHCH ₃)CN (85)	761
"	4-C ₆ H ₅ C ₆ H ₄ CH(CH ₂ CH=CHCH ₃)CN (75)	775
"	4-C ₆ H ₅ C ₆ H ₄ CH(C ₆ H ₅ - <i>n</i>)CN (84)	755
—	C ₆ H ₅ C[(CH ₂) ₂ N(C ₂ H ₅) ₂](C ₆ H ₅ - <i>n</i>)CN (80)	76
C ₆ H ₆	C ₆ H ₅ C(C ₆ H ₁₁)(CH ₂ CO ₂ C ₂ H ₅)CN (50-60)	630,752
Et ₂ O	C ₆ H ₅ C(C ₆ H ₁₁)(C ₆ H ₅ - <i>i</i>)CN (45)	343
Toluene	C ₆ H ₅ C(C ₆ H ₁₁)[(CH ₂) ₂ N(CH ₂) ₂]CN (60)	663
—	(C ₆ H ₅) ₂ C(C ₆ H ₅ - <i>n</i>)CN (94)	67
C ₆ H ₆	(C ₆ H ₅) ₂ C(CN)[(CH ₂) ₄ Cl]CN I (60), [(C ₆ H ₅) ₂ C(CN)(CH ₂) ₂] ₂ II (35)	700-702, 776
Toluene	I (—)	663
Et ₂ O	I (56)	549
—	(C ₆ H ₅) ₂ C[(CH ₂) ₄ Br]CN (79), II (13)	693-695
—	II (75)	756,763
THF	II (54)	198
—	(C ₆ H ₅) ₂ C[CH ₂ CH(CH ₃)CH ₂ Cl]CN (—)	614
C ₆ H ₆	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CHBrCH ₃]CN (32), (C ₆ H ₅) ₂ C(CN)(CH ₂) ₂ CH(CH ₃)C(CN)(C ₆ H ₅) ₂ (25)	777
—	(C ₆ H ₅) ₂ C(CH ₂ OC ₂ H ₅ - <i>i</i>)CN (88)	72
C ₆ H ₆	(C ₆ H ₅) ₂ C(CH ₂ CO ₂ C ₂ H ₅)CN (—)	778
—	" (—)	779
NH ₃ , Et ₂ O	(C ₆ H ₅) ₂ C(CH ₂ CO ₂ H)CN (72) ^a	654
—	(C ₆ H ₅) ₂ C(CHClCO ₂ C ₂ H ₅)CN (60)	773
DME	(C ₆ H ₅) ₂ C(CHCl ₂)CN (—)	780
C ₆ H ₆	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CN]CN I (50)	781
—	I (74)	73
C ₆ H ₆	I (42)	782
		783-785, 779
C ₂ H ₅ OH	[(C ₆ H ₅) ₂ C(CN)] ₂ CH ₂ (14-33)	786
Toluene	 (27)	787
C ₆ H ₆	1-C ₁₀ H ₇ C(C ₂ H ₅)[(CH ₂) ₂ N(CH ₂) ₂]CN (95)	740
Toluene	 (—)	635,752
—	(2-C ₃ H ₄ N)C(CH ₂ C ₆ H ₅)[(CH ₂) ₂ N(CH ₂) ₂]CN (67)	575
—	9- <i>n</i> -Butyl-9-cyanofluorene (—)	758
CH ₃ OH	9- <i>tert</i> -Butyl-9-cyanofluorene (8)	757
—	C ₆ H ₅ C[(CH ₂) ₂ N(C ₂ H ₅) ₂](C ₆ H ₁₁ - <i>i</i>)CN (66)	76
—	4-C ₆ H ₅ C ₆ H ₄ CH(C ₆ H ₁₁ - <i>i</i>)CN (85)	775
Et ₂ O	4-C ₆ H ₅ C ₆ H ₄ CH(C ₆ H ₁₁ - <i>n</i>)CN (85)	755
—	4-C ₆ H ₅ OC ₆ H ₄ CH(C ₂ H ₁₁ - <i>n</i>)CN (80)	761
—	4-C ₆ H ₅ OC ₆ H ₄ CH(C ₂ H ₁₁ - <i>i</i>)CN (84)	761
—	4-C ₆ H ₅ OC ₆ H ₄ CH(CN)CH ₂  (—)	635
—	(C ₆ H ₅) ₂ C(C ₆ H ₁₁ - <i>n</i>)CN (94)	67

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₄ (Contd.)	(C ₆ H ₅) ₂ CHCN	Cl(CH ₂) ₂ Cl	NaNH ₂
		Br(CH ₂) ₂ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	NaNH ₂
		(CH ₂) ₂ C(NO ₂)(CH ₂) ₂ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		Cl(CH ₂) ₄ CN	"
		"	NaNH ₂
		Br(CH ₂) ₄ CN	"
		(CH ₂) ₂ NCH ₂ CH(CH ₂)Cl	"
		"	C ₁₀ H ₈ Na
		CH ₃ CHBrCO ₂ C ₂ H ₅	NaNH ₂
		CH ₃ CHBr(CH ₂) ₂ CN	"
		Br(CH ₂) ₂ CO ₂ C ₂ H ₅ (?)	"
		(CH ₂) ₂ C ₂ CHCH ₂ Br	<i>t</i> -C ₄ H ₉ OK
			C ₁₀ H ₈ Na
		2-(1-Naphthyl)butyronitrile	(CH ₂) ₂ NCH ₂ CH(CH ₂)Cl
C ₆ H ₅ CH(C ₆ H _{13-n})CN	(C ₂ H ₅ O) ₂ CHCH ₂ Br	"	
C ₆ H ₅ CH[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN	BrCH ₂ CO ₂ C ₆ H _{5-t}	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
C ₆ H ₅ CH(C ₆ H ₁₁)CN	(C ₂ H ₅ O) ₂ CHCH ₂ Br	NaNH ₂	
(C ₆ H ₅) ₂ CHCN	<i>n</i> -C ₆ H ₁₃ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
	C ₆ H ₅ ·I	C ₁₀ H ₈ Na	
	Br(CH ₂) ₆ Br	NaNH ₂	
	"	"	
	CH ₃ CH[O(CH ₂) ₂ Cl] ₂	C ₁₀ H ₈ Na	
	(C ₂ H ₅ O) ₂ CHCH ₂ Br	NaNH ₂	
	(C ₂ H ₅) ₂ N(CH ₂) ₂ Cl	NaOC ₂ H ₅	
	1-(2-Chloroethyl)pyrrolidine	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
	1-Methyl-3-chloropiperidine	KOH	
	4-(2-Chloroethyl)morpholine	NaNH ₂	
	BrCH ₂ CO ₂ C ₆ H _{5-t}	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
	C ₂ H ₅ CHBrCO ₂ C ₂ H ₅	NaNH ₂	
	(CH ₂) ₂ CBrCO ₂ C ₂ H ₅	"	
	Br(CH ₂) ₂ CN	"	
2-(1-Naphthyl)butyronitrile	4-(2-Chloroethyl)morpholine	"	
C ₆ H ₅ CH(C ₆ H _{13-n})CN	C ₆ H ₅ CH ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
C ₆ H ₅ CH[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN	"	70% aq NaOH	
	(C ₂ H ₅) ₂ N(CH ₂) ₂ Cl	"	
C ₆ H ₅ CH(C ₆ H ₁₁)CN	<i>N</i> -(3-Bromopropyl)succinimide	NaNH ₂	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

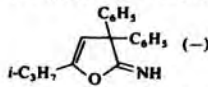
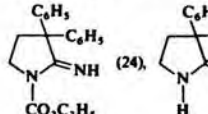
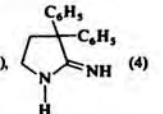
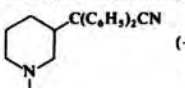
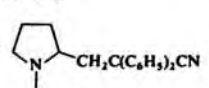
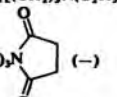
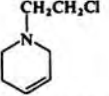

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ H ₆	(C ₆ H ₅) ₂ C[(CH ₂) ₂ Cl]CN (48)	702,776
—	(C ₆ H ₅) ₂ C[(CH ₂) ₂ Br]CN I (72), ((C ₆ H ₅) ₂ C(CN)CH ₂) ₂ CH ₂ II (16)	693-695
C ₆ H ₆	I (48), II (45)	700,701, 756,763
—	(C ₆ H ₅) ₂ C[(CH ₂) ₂ C(CH ₃) ₂ NO ₂]CN (81)	74
—	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CN]CN (78)	73
—	" (-)	784
C ₆ H ₆	" (79)	769,783
C ₆ H ₆ , dibenzo-18-crown-6	(C ₆ H ₅) ₂ C(CN)CH(CH ₃)CH ₂ N(CH ₃) ₂ I, (C ₆ H ₅) ₂ C(CN)CH(CH ₃)CH ₂ N(CH ₃) ₂ II, (86, I:II = 72:28)	788
THF	I (42), II (31)	198
C ₆ H ₆	(C ₆ H ₅) ₂ C[CH(CH ₃)CO ₂ C ₂ H ₅]CN (87, crude)	789
DMF	(C ₆ H ₅) ₂ C[CH(CH ₃)(CH ₂) ₂ CN]CN (-)	777
	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CO ₂ C ₂ H ₅]CN (-)	779
<i>t</i> -C ₄ H ₉ OH	 (-)	774
THF	 (24),  (4)	183
C ₆ H ₆	1-C ₁₀ H ₇ C(C ₂ H ₅)[CH(CH ₃)CH ₂ N(CH ₃) ₂]CN (-)	740
Et ₂ O	C ₆ H ₅ C(C ₆ H _{13-n})[CH ₂ CH(OC ₂ H ₅) ₂]CN (82-85)	637,638
—	C ₆ H ₅ C[(CH ₂) ₂ N(C ₂ H ₅) ₂][CH ₂ CO ₂ C ₆ H _{5-t}]CN (80)	78
Et ₂ O	C ₆ H ₅ C(C ₆ H ₁₁)[CH ₂ CH(OC ₂ H ₅) ₂]CN (80)	637,686,725
	(C ₆ H ₅) ₂ C(C ₆ H _{13-n})CN (92)	67
THF	(C ₆ H ₅) ₂ C(C ₆ H ₁₁)CN (71)	198
	(C ₆ H ₅) ₂ C[(CH ₂) ₆ Br]CN I (51)	702
C ₆ H ₆	I (51), [(C ₆ H ₅) ₂ C(CN)(CH ₂) ₂] (33)	700,701
THF	[(C ₆ H ₅) ₂ C(CN)CH ₂ CH ₂ O]CHCH ₃ (52)	198
Et ₂ O	(C ₆ H ₅) ₂ C[CH ₂ CH(OC ₂ H ₅) ₂]CN (80)	686,637,725
Toluene	(C ₆ H ₅) ₂ C[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN (95)	790,791
—	" (85)	67
CH ₃ COC ₂ H ₅	(C ₆ H ₅) ₂ C[(CH ₂) ₂ N(CH ₂) ₄]CN (35)	792
Toluene	 (-),  (-)	793
CH ₃ COC ₂ H ₅	(C ₆ H ₅) ₂ C(CN)(CH ₂) ₂ N ₂ O (82)	792
—	(C ₆ H ₅) ₂ C(CH ₂ CO ₂ C ₆ H _{5-t})CN (97)	78
C ₆ H ₆	(C ₆ H ₅) ₂ C[CH(CH ₃)CO ₂ C ₂ H ₅]CN (83, crude)	789
"	(C ₆ H ₅) ₂ C[CH(CH ₃)CO ₂ H]CN (35)	252
"	(C ₆ H ₅) ₂ C[CH(CH ₃)CO ₂ C ₂ H ₅]CN (50-55)	794
"	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CN]CN (83, crude)	795,779, 783,796
C ₆ H ₆	1-C ₁₀ H ₇ C(C ₂ H ₅)(CN)(CH ₂) ₂ N ₂ O (74)	740
—	C ₆ H ₅ C(C ₆ H _{13-n})(CH ₂ C ₆ H ₅)CN (32)	68
—	C ₆ H ₅ C[(CH ₂) ₂ N(C ₂ H ₅) ₂](CH ₂ C ₆ H ₅)CN (88)	76
	C ₆ H ₅ C[(CH ₂) ₂ N(C ₂ H ₅) ₂][(CH ₂) ₂ N(C ₂ H ₅) ₂]CN (34)	76
C ₆ H ₆ , DMF	 (-)	643

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₆ (Contd.)	C ₆ H ₅ CH(C ₆ H ₁₁)CN	(C ₂ H ₅ O) ₂ CH(CH ₂) ₂ Cl	"
		[(CH ₃) ₂ NCH ₂] ₂ CHCl	"
	(C ₆ H ₅) ₂ CHCN	C ₆ H ₅ CH ₂ Cl	KNH ₂
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		C ₆ H ₅ CH ₂ Br	C ₁₀ H ₈ Na
	"	C ₆ H ₅ CHCl ₂	30% aq NaOH, ethylpyridinium iodide, or 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	"	(C ₂ H ₅ O) ₂ CH(CH ₂) ₂ Cl	NaNH ₂
	"	(C ₂ H ₅ O) ₂ CHCH(CH ₃)Br	"
	"	(CH ₃) ₂ NCH ₂ C(CH ₃) ₂ CH ₂ Cl	LiNH ₂
	"	[(CH ₃) ₂ NCH ₂] ₂ CHCl	"
	"	1-Isopropyl-3-chloropyrrolidine	NaNH ₂
	"	1-(2-Chloroethyl)piperidine	KOH
	"		"
	"	1-(2-Chloroethyl)-4-methylpiperazine	NaNH ₂
	"	Br(CH ₂) ₄ CO ₂ C ₂ H ₅	"
"	<i>i</i> -C ₃ H ₇ CHBrCO ₂ C ₂ H ₅	"	
"	<i>n</i> -C ₇ H ₇ CHBrCO ₂ C ₂ H ₅	"	
"	Br(CH ₂) ₆ CN	"	
"	N-(3-Bromopropyl)succinimide	"	
"	1-Isopropyl-3-azetidinol methanesulfonate	NaH	
4-ClC ₆ H ₄ CH(C ₆ H ₅)CN	1-(2-Chloroethyl)piperidine	NaNH ₂	
2-(1-Naphthyl)butyronitrile	"	LiNH ₂	
"	"	NaNH ₂	
3-(2-Furyl)-2-phenylbutyronitrile	"	KNH ₂	
	C ₆ H ₅ CH ₂ Cl	NaNH ₂	
9-Cyanofluorene	C ₆ H ₅ CH ₂ Cl or C ₆ H ₅ CH ₂ Br	NaOCH ₃ or <i>t</i> -C ₄ H ₉ OK	
"	C ₆ H ₅ CH ₂ Cl	KH	
"	ZC ₆ H ₄ CH ₂ X	<i>t</i> -C ₄ H ₉ OK	
"	"	NaOCH ₃	
"	"	"	
4-C ₆ H ₅ C ₆ H ₄ CH ₂ CN	<i>n</i> -C ₆ H ₁₁ Br	NaNH ₂	
"	(<i>i</i> -C ₃ H ₇) ₂ N(CH ₂) ₂ Cl	"	
(C ₆ H ₅) ₂ CHCN	C ₆ H ₅ (CH ₂) ₂ Cl	KNH ₂	
"	C ₆ H ₅ (CH ₂) ₂ Br	C ₁₀ H ₈ Na	
"	"	NaNH ₂	
"	"	NaH	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)



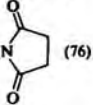
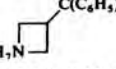
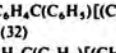
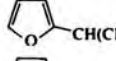
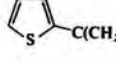
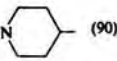
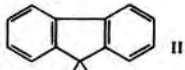



Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₂ O, C ₆ H ₆	C ₆ H ₅ C(C ₆ H ₁₁)[(CH ₂) ₂ CH(OC ₂ H ₅) ₂]CN (72)	644,645
Toluene	C ₆ H ₅ C(C ₆ H ₁₁)[(CH ₂) ₂ CH(OC ₂ H ₅) ₂]CN (-)	665
NH ₃ , Et ₂ O	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CH(OC ₂ H ₅) ₂]CN (95-99)	538,260
-	" (98)	67
THF	" (76)	198
-	(C ₆ H ₅) ₂ C(CHClC ₆ H ₅)CN (-)	615,693
Et ₂ O, C ₆ H ₆	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CH(OC ₂ H ₅) ₂]CN (75)	644,645
C ₆ H ₆ or toluene	(C ₆ H ₅) ₂ C[CH(CH ₃)CH(OC ₂ H ₅) ₂]CN (75-80)	797,798
Toluene	(C ₆ H ₅) ₂ C[CH ₂ C(CH ₃) ₂ CH ₂ N(CH ₃) ₂]CN (73)	663
"	(C ₆ H ₅) ₂ C[CH(CH ₂ N(CH ₃) ₂) ₂]CN (-)	665
"	2-(1-Isopropyl-3-pyrrolidyl)-2,2-diphenylacetone nitrile (-)	799
CH ₃ COC ₂ H ₅	(C ₆ H ₅) ₂ C[(CH ₂) ₂ N(CH ₂) ₂]CN (28)	792
"	(C ₆ H ₅) ₂ C(CN)(CH ₂) ₂ N  (12)	792
C ₆ H ₆	(C ₆ H ₅) ₂ C(CN)(CH ₂) ₂ N  (-)	776
"	(C ₆ H ₅) ₂ C[(CH ₂) ₄ CO ₂ H]CN (66)*	769,779
"	(C ₆ H ₅) ₂ C[CH(C ₂ H ₅ - <i>i</i>)CO ₂ C ₂ H ₅]CN (85, crude)	800
"	(C ₆ H ₅) ₂ C[CH(C ₂ H ₅ - <i>n</i>)CO ₂ C ₂ H ₅]CN (90-95, crude)	789
"	(C ₆ H ₅) ₂ C[(CH ₂) ₆ CN]CN (-)	795
C ₆ H ₆ , DMF	(C ₆ H ₅) ₂ C(CN)(CH ₂) ₂ N  (76)	643
Toluene	 (56)	787
-	<i>i</i> -C ₃ H ₇ N 	
-	4-ClC ₆ H ₄ CH(C ₆ H ₅)[(CH ₂) ₂ N(CH ₂) ₂]CN (32)	662
Toluene	" (32)	663
-	1-C ₁₀ H ₇ C(C ₂ H ₅)[(CH ₂) ₂ N(CH ₂) ₂]CN (42)	97
C ₆ H ₆	" (89)	740
Toluene	 CH(CH ₃)C(C ₆ H ₅)[(CH ₂) ₂ N(CH ₂) ₂]CN (-)	753
-	 C(CH ₂ C ₆ H ₅)(CN)(CH ₂) ₂ N  (90)	567
CH ₃ OH or <i>i</i> -C ₄ H ₉ OH	9-Benzyl-9-cyanofluorene (ca. 95)	138,801,802
DMSO	" (-)	137
	ZC ₆ H ₄ CH ₂ CN	
<i>i</i> -C ₄ H ₉ OH or CH ₃ OH	II, Z = 4-Br, X = Br (-)	801
"	II, Z = 3-Br, X = Br (-)	138
"	II, Z = 3-Cl, X = Br (-)	138
"	II, Z = 3-NO ₂ , X = Br or Cl (-)	138
Et ₂ O	4-C ₆ H ₅ C ₆ H ₄ CH(C ₆ H ₁₁ - <i>n</i>)CN (82)	755
Toluene	4-C ₆ H ₅ C ₆ H ₄ CH[(CH ₂) ₂ N(C ₂ H ₅ - <i>i</i>) ₂]CN (-)	803
NH ₃ , Et ₂ O	(C ₆ H ₅) ₂ C[(CH ₂) ₂ C ₆ H ₅]CN (89)	260
THF	" (65)	198
NH ₃ , Et ₂ O	" (64)	162
DME	" (60)	162

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₄ (Contd.)	C ₆ H ₅ (CH ₂) ₂ Br	C ₆ H ₅ CH(CH ₂)Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		"	KNH ₂
		C ₆ H ₅ O(CH ₂) ₂ Br	LiN(C ₂ H ₅) ₂
		(C ₂ H ₅ O) ₂ CHCH(C ₂ H ₅)Br	NaNH ₂
		(CH ₂) ₂ N(CH ₂) ₂ OCO ₂ C ₂ H ₅	KOAc
		1-Isobutyl-3-chloropyrrolidine	NaNH ₂
			"
		"	KOH
		n-C ₄ H ₉ CHBrCO ₂ C ₂ H ₅	"
		N-(4-Bromobutyl)succinimide	NaNH ₂
9-Cyanofluorene	ZC ₆ H ₄ CH ₂ X	ZC ₆ H ₄ CH ₂ X	NaOCH ₃
			"
C ₆ H ₅ CH(C ₆ H ₁₁)CN (C ₆ H ₅) ₂ CHCN	C ₆ H ₅ CO ₂ (CH ₂) ₂ Br	C ₆ H ₅ CO ₂ (CH ₂) ₂ Br	"
		"	"
		(C ₂ H ₅ O) ₂ CHCH(C ₂ H ₅ -n)Br	"
		Br(CH ₂) ₆ CO ₂ C ₂ H ₅	"
		"	"
		[(CH ₂) ₂ N(CH ₂) ₂ O] ₂ CO	CH ₃ CO ₂ K
		(C ₂ H ₅) ₂ NCH ₂ C(CH ₂) ₂ CH ₂ Cl	LiNH ₂
		N-(5-Bromopentyl)succinimide	NaNH ₂
		"	"
		"	KOH
9-Cyanoanthene (C ₆ H ₅) ₂ CHCN	Br(CH ₂) ₂ CO ₂ C ₂ H ₅		"
		"	"
			"
		"	"
		[(CH ₂) ₂ N(CH ₂) ₂ O] ₂ CO	"
		Br(CH ₂) ₂ CO ₂ C ₂ H ₅	NaNH ₂
		"	"
		Br(CH ₂) ₂ CH(CO ₂ C ₂ H ₅) ₂	"
		Br(CH ₂) ₂ C(CH ₂) ₂ (CO ₂ C ₂ H ₅) ₂	"
		Br(CH ₂) ₁₀ Br	"
1-Cyclohexyl-3-azetidin methanesulfonate	C ₆ H ₅ O) ₂ CHCH(C ₆ H ₅ -n)Br	(C ₂ H ₅) ₂ NCH ₂ C(CH ₂) ₂ CH ₂ Cl	LiNH ₂
		Br(CH ₂) ₆ CN	NaNH ₂
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	"
		"	NaH

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)


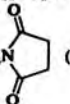
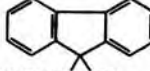
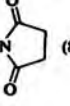
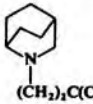


Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	(C ₆ H ₅) ₂ C[CH(CH ₂)C ₆ H ₅]CN (96)	67
NH ₃ , Et ₂ O	" (88)	260
C ₆ H ₆	(C ₆ H ₅) ₂ C[(CH ₂) ₂ OC ₆ H ₅]CN (87)	562
"	(C ₆ H ₅) ₂ C[CH(C ₂ H ₅)CH(OC ₂ H ₅) ₂]CN (75-80)	797
—	(C ₆ H ₅) ₂ C[(CH ₂) ₂ N(CH ₂) ₂]CN (—)	748
Toluene	2-(1-Isobutyl-3-pyrrolidyl)-2,2-diphenylacetonitrile (—)	799
CH ₃ CO ₂ H ₃	 (66)	792
"	(C ₆ H ₅) ₂ C[CH(C ₆ H ₅ -n)CO ₂ C ₂ H ₅]CN (90, crude)	789
"	(C ₆ H ₅) ₂ C[(CH ₂) ₂ NH ₂]CO ₂ H (—) ^p	659,660
C ₆ H ₆ , DMF	(C ₆ H ₅) ₂ C(CN)(CH ₂) ₂ N  (60)	661
CH ₃ OH	 ZC ₆ H ₄ CH ₂ CN I, Z = 3-OCH ₃ , X = Cl (—) I, Z = 3-CH ₃ , X = Br (—) I, Z = 4-CH ₃ , X = Br or Cl (—)	138
"	C ₆ H ₅ C(C ₆ H ₁₁)[(CH ₂) ₂ OCOC ₆ H ₅]CN (35)	714,715
"	(C ₆ H ₅) ₂ C[(CH ₂) ₂ OCOC ₆ H ₅]CN (35)	714,715
C ₆ H ₆	(C ₆ H ₅) ₂ C[CH(C ₂ H ₅ -n)CH(OC ₂ H ₅) ₂]CN (75-80)	797
"	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CO ₂ H]CN (80) ^p	795
—	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CO ₂ C ₂ H ₅]CN (—)	779
Toluene	(C ₆ H ₅) ₂ C[(CH ₂) ₂ N(CH ₂) ₂]CN (—)	748
—	(C ₆ H ₅) ₂ C[CH ₂ C(CH ₂) ₂ CH ₂ N(C ₂ H ₅) ₂]CN (66)	663
—	(C ₆ H ₅) ₂ C[(CH ₂) ₂ NH ₂]CO ₂ H (—) ^p	659,660
C ₆ H ₆ , DMF	(C ₆ H ₅) ₂ C(CN)(CH ₂) ₂ N  (80)	661
CH ₃ CO ₂ H ₃	 (64)	792
"	(CH ₂) ₂ C(C ₆ H ₅) ₂ CN	
"	 (40)	792
"	N(CH ₂) ₂ C(C ₆ H ₅) ₂ CN	
"	9-(2-Dimethylamino)ethyl-9-cyanoanthene hydrochloride (—)	748
C ₆ H ₆	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CO ₂ H]CN (72) ^p	795
"	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CO ₂ C ₂ H ₅]CN (—)	779
C ₆ H ₆	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CO ₂ H]CN (—) ^p	769,770
DMF	(C ₆ H ₅) ₂ C[(CH ₂) ₂ C(CH ₂) ₂ (CO ₂ C ₂ H ₅) ₂]CN (63, crude)	777,804
C ₆ H ₆	[(C ₆ H ₅) ₂ C(CN)(CH ₂) ₂] ₂ I (63)	805
"	(C ₆ H ₅) ₂ C[(CH ₂) ₁₀ Br]CN (65), I (10)	700
"	(C ₆ H ₅) ₂ C[CH(C ₆ H ₅ -n)CH(OC ₂ H ₅) ₂]CN (75-80)	797
Toluene	(C ₆ H ₅) ₂ C[CH ₂ C(CH ₂) ₂ N(CH ₂) ₂]CN (61)	663
C ₆ H ₆	(C ₆ H ₅) ₂ C[(CH ₂) ₂ CN]CN (60)	805,806
Toluene	 (18)	787

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₄ (Contd.)	(C ₆ H ₅) ₂ CHCN	<i>N</i> -(6-Bromohexyl)succinimide	NaNH ₂
		"	"
	2-(1-Naphthyl)butyronitrile C ₆ H ₅ CH(C ₆ H ₁₃ - <i>n</i>)CN	(CH ₃) ₂ NCH ₂ CH(C ₆ H ₅)Cl [(C ₂ H ₅) ₂ NCH ₂] ₂ CHCl	" "
	C ₆ H ₅ CH(C ₆ H ₁₁)CN	<i>N</i> -(3-Bromopropyl)phthalimide	"
		[(C ₂ H ₅) ₂ NCH ₂] ₂ CHCl	"
		1,3-Bis-(4-morpholinyl)-2-chloropropane	"
	(C ₆ H ₅) ₂ CHCN	Br(CH ₂) ₁₀ CN Br(CH ₂) ₁₁ CO ₂ C ₂ H ₅ Br(CH ₂) ₂ C(C ₂ H ₅)(CO ₂ C ₂ H ₅) ₂ [(C ₂ H ₅) ₂ NCH ₂] ₂ CHCl	" " " "
		<i>N</i> -(3-Bromopropyl)phthalimide	"
	4-ClC ₆ H ₄ CH(C ₆ H ₅)CN (C ₆ H ₅) ₂ CHCN	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHCl Br(CH ₂) ₁₁ Br	" "
		1-(1-Phenylethyl)-3-azetidinol methanesulfonate	NaH
3,4-(CH ₂ O) ₂ C ₆ H ₃ CH(C ₆ H ₅ - <i>i</i>)CN C ₆ H ₅ CH(C ₆ H ₁₁)CN (C ₆ H ₅) ₂ CHCN	3,4-(CH ₂ O) ₂ C ₆ H ₃ (CH ₂) ₂ N(CH ₃)(CH ₂) ₂ Cl	NaNH ₂	
	1,3-Bis(1-piperidyl)-2-chloropropane (C ₆ H ₅) ₂ CHCl	" KNH ₂	
		50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
		KOH	
9-Cyanofluorene	(C ₆ H ₅) ₂ CHCl	<i>i</i> -C ₄ H ₉ OK	
	9-Chlorofluorene	"	
3,4-(CH ₂ O) ₂ C ₆ H ₃ CH(C ₆ H ₅ - <i>i</i>)CN (C ₆ H ₅) ₂ CHCN	3,4-(CH ₂ O) ₂ C ₆ H ₃ (CH ₂) ₂ N(CH ₃)(CH ₂) ₂ Cl	NaNH ₂	
	Br(CH ₂) ₁₁ CO ₂ CH ₃	"	
	3,4-(CH ₂ O) ₂ C ₆ H ₃ (CH ₂) ₂ N(CH ₃)(CH ₂) ₂ Cl	"	
	<i>N</i> -(10-Bromodecyl)succinimide	"	
	"	"	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

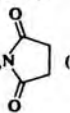
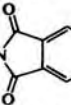

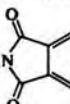


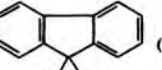
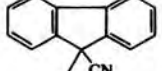
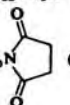
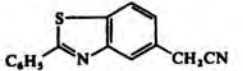
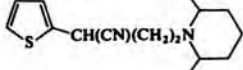
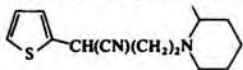
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	(C ₆ H ₅) ₂ C[(CH ₂) ₆ NH ₂]CO ₂ H (—) ^a	659,660
C ₆ H ₆ , DMF	(C ₆ H ₅) ₂ C(CN)(CH ₂) ₆  (80)	661
C ₆ H ₆ Toluene	1-C ₁₀ H ₇ C(C ₂ H ₅)[CH(C ₆ H ₅)CH ₂ N(CH ₃) ₂]CN (72) C ₆ H ₅ C(C ₆ H ₁₁ - <i>n</i>)[CH(CH ₂ N(C ₂ H ₅) ₂)]CN (—)	740 665
C ₆ H ₆ , DMF	C ₆ H ₅ C(C ₆ H ₁₁)(CN)(CH ₂) ₂  (54)	643
Toluene	C ₆ H ₅ C(C ₆ H ₁₁)[CH[CH ₂ N(C ₂ H ₅) ₂]]CN (—)	611,665
"	C ₆ H ₅ C(C ₆ H ₁₁)(CN)CH(CH ₂) ₂  (—)	665
C ₆ H ₆ DMF Toluene	(C ₆ H ₅) ₂ C[(CH ₂) ₁₀ CN]CN (59) (C ₆ H ₅) ₂ C[(CH ₂) ₆ CO ₂ C ₂ H ₅]CN (57) (C ₆ H ₅) ₂ C[(CH ₂) ₂ C(C ₂ H ₅)(CO ₂ C ₂ H ₅)]CN (—) (C ₆ H ₅) ₂ C[CH(CH ₂ N(C ₂ H ₅) ₂)]CN (—)	807,805 805,806 804 665
C ₆ H ₆ , DMF	(C ₆ H ₅) ₂ C(CN)(CH ₂) ₂  (75)	643,716
Toluene C ₆ H ₆	4-ClC ₆ H ₄ C(C ₆ H ₅)[CH[CH ₂ N(C ₂ H ₅) ₂]]CN (—) (C ₆ H ₅) ₂ C[(CH ₂) ₁₂ Br]CN (32), [(C ₆ H ₅) ₂ C(CN)(CH ₂) ₆] ₂ (19)	665 700
Toluene	 C(C ₆ H ₅) ₂ CN (42)	787
"	3,4-(CH ₂ O) ₂ C ₆ H ₃ C(C ₆ H ₅ - <i>i</i>)[(CH ₂) ₂ N(CH ₃)(CH ₂) ₂ C ₆ H ₃ (OCH ₃) ₂ -3,4]CN (66)	717
"	C ₆ H ₅ C(C ₆ H ₁₁)[CH[CH ₂ N(CH ₂) ₃]]CN (—)	665
NH ₃ , Et ₂ O	(C ₆ H ₅) ₂ C[CH(C ₆ H ₅) ₂]CN (96)	260
—	" (96)	67
CH ₂ CO ₂ C ₂ H ₅	(C ₆ H ₅) ₂ C(CN)(CH ₂) ₂  (52)	792
<i>i</i> -C ₄ H ₉ OH	 (—) (C ₆ H ₅) ₂ CHCN	801
"	 (—)	801
Toluene C ₆ H ₆ Toluene	3,4-(CH ₂ O) ₂ C ₆ H ₃ C(C ₆ H ₅ - <i>i</i>)[(CH ₂) ₂ N(CH ₃)(CH ₂) ₂ C ₆ H ₃ (OCH ₃) ₂ -3,4]CN (70) (C ₆ H ₅) ₂ C[(CH ₂) ₁₁ CO ₂ CH ₃]CN (83) (C ₆ H ₅) ₂ C[(CH ₂) ₂ N(CH ₃)(CH ₂) ₂ C ₆ H ₃ (OCH ₃) ₂ -3,4]CN (72) (C ₆ H ₅) ₂ C[(CH ₂) ₁₀ NH ₂]CO ₂ H (—) ^a	717 805,807 717 659,660
C ₆ H ₆ , DMF	(C ₆ H ₅) ₂ C(CN)(CH ₂) ₁₀  (85)	661

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₄ (Contd.)	(C ₆ H ₅) ₂ CHCN	[FeCH ₂ N(CH ₃) ₂]I N-(12-Bromododecyl)succinimide	Na NaNH ₂
		"	"
		Br(CH ₂) ₂ C(C ₆ H ₅)(CO ₂ C ₂ H ₅) ₂ (C ₆ H ₅) ₂ CClCN	" 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
C ₁₃	(<i>n</i> -C ₄ H ₉) ₂ Sn(CH ₂) ₂ CN C ₆ H ₅ CH ₂ CH(C ₆ H ₅)CN	CH ₃ I "	LDA NaH
	2-ClC ₆ H ₄ CH ₂ CH(C ₆ H ₅)CN 3,4-Cl ₂ C ₆ H ₃ CH ₂ CH(C ₆ H ₅)CN 4-(C ₆ H ₅ CH ₂)C ₆ H ₄ CH ₂ CN 3-(C ₆ H ₅ CO)C ₆ H ₄ CH ₂ CN	" " " " CH ₃ I	NaNH ₂ or CH ₃ MgI " " NaNH ₂ (<i>n</i> -C ₄ H ₉) ₄ NOH
		"	NaNH ₂
		CH ₃ I ^r	"
	4-C ₆ H ₅ CH ₂ C ₆ H ₄ CH ₂ CN	C ₂ H ₅ Br	"
	2,5-CH ₂ O(C ₆ H ₅)C ₆ H ₃ CH ₂ CN	"	"
	3-(C ₆ H ₅ CH ₂ O)C ₆ H ₄ CH ₂ CN C ₆ H ₅ CH(CN)(CH ₂) ₂ N(CH ₃) ₂ C ₆ H ₅ CH ₂ CH(C ₆ H ₅)CN	" " Cl(CH ₂) ₂ Br	" " "
	4-(C ₆ H ₅ CH ₂)C ₆ H ₄ CH ₂ CN C ₆ H ₅ CH(CN)(CH ₂) ₂ N(CH ₃) ₂	HC≡CCH ₂ Br CH ₂ =CHCH ₂ Br ^r <i>i</i> -C ₃ H ₇ Br ^r	" " "
		RX ^r	"
	(<i>n</i> -C ₄ H ₉) ₂ Sn(CH ₂) ₂ CN	CH ₂ =C(CH ₃)CH ₂ Cl	LDA
	C ₆ H ₅ CH ₂ CH(C ₆ H ₅)CN	Cl(CH ₂) ₂ Cl	NaNH ₂
	3-Methyl-2-(1-naphthyl)butyronitrile	(CH ₃) ₂ N(CH ₂) ₂ Cl "	" "
	3-(2-Furyl)-2-phenylvaleronitrile	"	KNH ₂
	C ₆ H ₅ CH[(CH ₂) ₂ N(CH ₃) ₂]CN C ₆ H ₅ CH ₂ CH(C ₆ H ₅)CN	<i>sec</i> -C ₄ H ₉ Br ^r Cl(CH ₂) ₂ Cl	NaNH ₂ "
	3-Methyl-2-(1-naphthyl)butyronitrile	Br(CH ₂) ₂ CO ₂ C ₂ H ₅ (CH ₃) ₂ NCH ₂ CH(CH ₂) ₂ Cl C ₂ H ₅ N(CH ₃)(CH ₂) ₂ Cl (C ₂ H ₅ O) ₂ CHCH ₂ Br C ₆ H ₁₁ I	" " " " C ₁₀ H ₈ Na

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

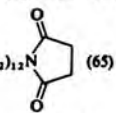
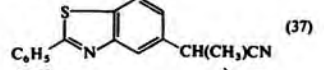
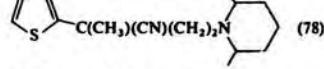
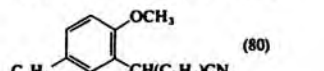
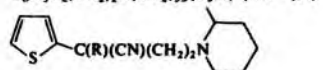
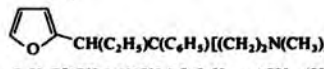
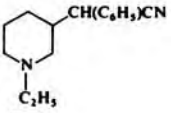
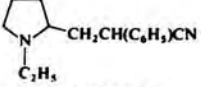

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Toluene, DMF —	(C ₆ H ₅) ₂ C(CH ₂ Fe)CN (76) (C ₆ H ₅) ₂ C[(CH ₂) ₁₂ NH ₂]CO ₂ H (—) ^r	667 659,660
C ₆ H ₆ , DMF	 (65)	661
C ₆ H ₆	(C ₆ H ₅) ₂ CH[(CH ₂) ₂ CH(C ₆ H ₅)CO ₂ H]CN (—) [(C ₆ H ₅) ₂ C(CN)] ₂ (91)	769,770 79
THF, -40°	(<i>n</i> -C ₄ H ₉) ₂ SnCH ₂ CH(CH ₃)CN (65), (<i>n</i> -C ₄ H ₉) ₂ SnCH ₂ C(CH ₃) ₂ CN (21)	164
—	C ₆ H ₅ CH ₂ C(C ₆ H ₅)(CH ₃)CN (71)	692
Et ₂ O	" (—)	51
"	2-ClC ₆ H ₄ CH ₂ C(C ₆ H ₅)(CH ₃)CN (—)	51
"	3,4-Cl ₂ C ₆ H ₃ CH ₂ C(C ₆ H ₅)(CH ₃)CN (—)	51
"	4-(C ₆ H ₅ CH ₂)C ₆ H ₄ CH(CH ₃)CN (84)	775
CH ₂ Cl ₂	3-C ₆ H ₅ COC ₆ H ₄ CH(CH ₃)CN I, 3-C ₆ H ₅ COC ₆ H ₄ C(CH ₃) ₂ CN II I:II = 8:2 (—)	808
C ₆ H ₆	 (37)	291
—	 (78)	567
Et ₂ O	4-C ₆ H ₅ CH ₂ C ₆ H ₄ CH(C ₂ H ₅)CN (91)	775
"	 (80)	775
—	3-C ₆ H ₅ CH ₂ OC ₆ H ₄ C(C ₂ H ₅) ₂ CN (—)	675
C ₆ H ₆	C ₆ H ₅ C[(CH ₂) ₂ N(CH ₃) ₂](C ₂ H ₅)CN (85)	681
"	C ₆ H ₅ CH ₂ C(C ₆ H ₅)[(CH ₂) ₂ Cl]CN (64), [C ₆ H ₅ CH ₂ C(C ₆ H ₅)(CN)CH ₂] ₂ CH ₂ (18)	700-702,72
Et ₂ O, C ₆ H ₆	C ₆ H ₅ CH ₂ C(C ₆ H ₅)(CH ₂ C≡CH)CN (60-88)	613
Et ₂ O	4-C ₆ H ₅ CH ₂ C ₆ H ₄ CH(CH ₂ CH=CH ₂)CN (75)	775
C ₆ H ₆	C ₆ H ₅ C[(CH ₂) ₂ N(CH ₃) ₂](C ₂ H ₅ - <i>i</i>)CN (86)	681
—		567
	I, R = C ₂ H ₅ - <i>i</i> (65) I, R = CH ₂ CH=CH ₂ (76)	
THF, -40°	(<i>n</i> -C ₄ H ₉) ₂ SnCH ₂ CH[CH ₂ C(CH ₃)=CH ₂]CN (72), (<i>n</i> -C ₄ H ₉) ₂ SnCH ₂ C[CH ₂ C(CH ₃)=CH ₂]CN (4)	164
C ₆ H ₆	C ₆ H ₅ CH ₂ C(C ₆ H ₅)[(CH ₂) ₂ Cl]CN (40), [C ₆ H ₅ CH ₂ C(C ₆ H ₅)(CN)CH ₂] ₂ CH ₂ (43)	700-702
NH ₃ , Et ₂ O	1-C ₁₀ H ₇ C(C ₂ H ₅ - <i>i</i>)[(CH ₂) ₂ N(CH ₃) ₂]CN (—)	621
C ₆ H ₆	" (—)	740
Toluene	 (—)	753
C ₆ H ₆	C ₆ H ₅ C[(CH ₂) ₂ N(CH ₃) ₂](C ₆ H ₅ - <i>sec</i>)CN (82)	681
"	C ₆ H ₅ CH ₂ C(C ₆ H ₅)[(CH ₂) ₂ Cl]CN (45), [C ₆ H ₅ CH ₂ C(C ₆ H ₅)(CN)CH ₂] ₂ CH ₂ (37)	700-702
"	C ₆ H ₅ CH ₂ C(C ₆ H ₅)[(CH ₂) ₂ CO ₂ H]CN (75) ^r	682
"	1-C ₁₀ H ₇ C(C ₂ H ₅ - <i>i</i>)[CH(CH ₃)CH ₂ N(CH ₃) ₂]CN (86)	740
"	1-C ₁₀ H ₇ C(C ₂ H ₅ - <i>i</i>)[(CH ₂) ₂ N(CH ₃) ₂]CN (85)	740
Et ₂ O	C ₆ H ₅ C(C ₂ H ₅ - <i>m</i>)[CH ₂ CH(OC ₂ H ₅) ₂]CN (82-85)	637,638
THF	C ₆ H ₅ CH ₂ C(C ₆ H ₅)(C ₆ H ₁₁)CN (—)	198

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₅ (Contd.)	C ₆ H ₅ CH ₂ CH(C ₆ H ₅)CN	Br(CH ₂) ₆ Br	NaNH ₂
		BrCH ₂ CO ₂ C ₆ H ₄ - <i>t</i> (C ₂ H ₅ O) ₂ CHCH ₂ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl NaNH ₂
	3-Methyl-2-(1-naphthyl)butyronitrile	4-(2-Chloroethyl)morpholine	"
		(C ₂ H ₅) ₂ N(CH ₂) ₂ Cl	"
		C ₆ H ₁₁ Br	KNH ₂
		"	"
	(<i>n</i> -C ₄ H ₉) ₃ Sn(CH ₂) ₂ CN	C ₆ H ₅ CH ₂ Br	LDA
	C ₆ H ₅ CH ₂ CH(C ₆ H ₅)CN	(C ₂ H ₅ O) ₂ CH(CH ₂) ₂ Cl 1-(2-Chloroethyl)piperidine	NaNH ₂ LiNH ₂
		1-(3-Bromopropyl)succinimide	NaNH ₂
	3-Methyl-2-(1-naphthyl)butyronitrile	1-(2-Chloroethyl)piperidine	"
3-(2-Furyl)-2-phenylvaleronitrile	"	KNH ₂	
	C ₆ H ₅ CH ₂ Cl ^a	NaNH ₂	
(<i>n</i> -C ₄ H ₉) ₃ Sn(CH ₂) ₂ CN	C ₆ H ₅ O(CH ₂) ₂ Br	LDA	
C ₆ H ₅ CH ₂ CH(C ₆ H ₅)CN	<i>N</i> -(4-Bromobutyl)succinimide	NaNH ₂	
	"	"	
(<i>n</i> -C ₄ H ₉) ₃ Sn(CH ₂) ₂ CN	(<i>E</i>)-C ₆ H ₅ CH=CHCH ₂ Br	LDA	
C ₆ H ₅ CH ₂ CH(C ₆ H ₅)CN	C ₆ H ₅ CO ₂ (CH ₂) ₂ Br	NaNH ₂	
3-Methyl-2-(1-naphthyl)butyronitrile	(CH ₂) ₂ NCH ₂ CH(C ₆ H ₅)Cl C ₆ H ₅ CH ₂ N(CH ₃)(CH ₂) ₂ Cl	" "	
(<i>n</i> -C ₄ H ₉) ₃ Sn(CH ₂) ₂ CN	1-(Chloromethyl)naphthalene	LDA	
4-XC ₆ H ₄ CH(C ₆ H ₁₁)CN	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHCl	NaNH ₂ "	
C ₆ H ₅ CH ₂ CH(C ₆ H ₅)CN	<i>N</i> -(3-Bromopropyl)phthalimide	"	

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)










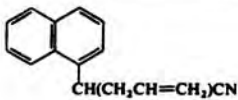
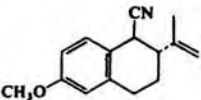
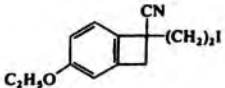
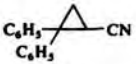
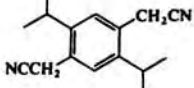
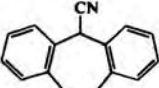
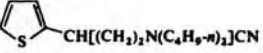
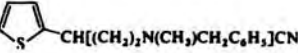
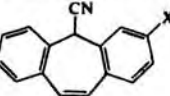
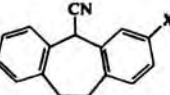
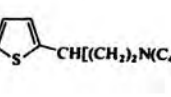
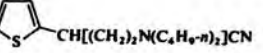
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ H ₆	C ₆ H ₅ CH ₂ C(C ₆ H ₅)[(CH ₂) ₆ Br]CN (45), [C ₆ H ₅ CH ₂ C(C ₆ H ₅)(CN)(CH ₂) ₂] ₂ (27)	700-702
Et ₂ O	C ₆ H ₅ CH ₂ C(C ₆ H ₅)(CH ₂ CO ₂ C ₆ H ₄ - <i>t</i>)CN (95) C ₆ H ₅ CH ₂ C(C ₆ H ₅)[CH ₂ CH(OC ₂ H ₅) ₂]CN (80)	78 686,637,725a
C ₆ H ₆	1-C ₁₀ H ₇ C(C ₃ H ₇ - <i>i</i>)(CN)(CH ₂) ₂ N  (67)	740
"	1-C ₁₀ H ₇ C(C ₃ H ₇ - <i>i</i>)[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN (91)	740
Toluene	 (—)	250,251
"	 CH ₂ C(C ₆ H ₅)(C ₆ H ₁₁)CN (—)	250,251
THF, -40°	(<i>n</i> -C ₄ H ₉) ₃ SnCH ₂ CH(CH ₂ C ₆ H ₅)CN (63), (<i>n</i> -C ₄ H ₉) ₃ SnCH ₂ C(CH ₂ C ₆ H ₅) ₂ CN (17)	164
Et ₂ O, C ₆ H ₆	C ₆ H ₅ CH ₂ C(C ₆ H ₅)[(CH ₂) ₂ CH(OC ₂ H ₅) ₂]CN (73)	644,645
Toluene	C ₆ H ₅ CH ₂ C(C ₆ H ₅)[(CH ₂) ₂ N(CH ₂) ₂]CN (33)	663
C ₆ H ₆ , DMF	C ₆ H ₅ CH ₂ C(C ₆ H ₅)(CN)(CH ₂) ₂ N  (—)	643
C ₆ H ₆	1-C ₁₀ H ₇ C(C ₃ H ₇ - <i>i</i>)[(CH ₂) ₂ N(CH ₂) ₂]CN (86)	740
Toluene	 CH(C ₂ H ₅)C(C ₆ H ₅)[(CH ₂) ₂ N(CH ₂) ₂]CN (—)	753
"	 C(CH ₂ C ₆ H ₅)(CN)(CH ₂) ₂ N  (76)	567
THF, -40°	(<i>n</i> -C ₄ H ₉) ₃ SnCH ₂ CH(CH ₂ CH ₂ OC ₆ H ₅)CN (70), (<i>n</i> -C ₄ H ₉) ₃ SnCH ₂ C(CH ₂ CH ₂ OC ₆ H ₅) ₂ CN (16)	164
"	C ₆ H ₅ CH ₂ C(C ₆ H ₅)[(CH ₂) ₂ NH ₂]CO ₂ H (—) ^b	659,660
C ₆ H ₆ , DMF	C ₆ H ₅ CH ₂ C(C ₆ H ₅)(CN)(CH ₂) ₂ N  (72)	661
THF, -40°	(<i>n</i> -C ₄ H ₉) ₃ SnCH ₂ CH(CH ₂ CH=CHC ₆ H ₅)CN (68), (<i>n</i> -C ₄ H ₉) ₃ SnCH ₂ C(CH ₂ CH=CHC ₆ H ₅) ₂ CN (6)	164
C ₆ H ₆ , DMF	C ₆ H ₅ CH ₂ C(C ₆ H ₅)[(CH ₂) ₂ OCOC ₆ H ₅]CN (47)	714,715
C ₆ H ₆	1-C ₁₀ H ₇ C(C ₃ H ₇ - <i>i</i>)[CH(C ₆ H ₅)CH ₂ N(CH ₃) ₂]CN (71)	740
"	1-C ₁₀ H ₇ C(C ₃ H ₇ - <i>i</i>)[(CH ₂) ₂ N(CH ₃) ₂]CN (78)	740
THF, -40°	(<i>n</i> -C ₄ H ₉) ₃ SnCH ₂ CH(CH ₂ C ₁₀ H ₇ -1)CN (69), (<i>n</i> -C ₄ H ₉) ₃ SnCH ₂ C(CH ₂ C ₁₀ H ₇ -1) ₂ CN (13)	164
Toluene	4-XC ₆ H ₄ C(C ₆ H ₁₁)[CH(CH ₂ N(C ₂ H ₅) ₂) ₂]CN I	665
"	I, X = CH ₃ (—) I, X = OCH ₃ (—)	665
C ₆ H ₆ , DMF	C ₆ H ₅ CH ₂ C(C ₆ H ₅)(CN)(CH ₂) ₂ N  (73)	643,716

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₅ (Contd.)		CH ₂ =CH(CH ₂) ₅ Cl	NaNH ₂
			"
C ₁₆		CH ₃ I	LDA
		"	"
	4-[C ₆ H ₅ (CH ₂) ₂] ₂ C ₆ H ₄ CH ₂ CN	CH ₃ I ^a C ₂ H ₅ Br	NaNH ₂
		(CH ₃) ₂ SO ₄	"
		RX ^c	"
		"	"
	C ₆ H ₅ (CH ₂) ₂ CH(C ₆ H ₅)CN (2-C ₁₀ H ₇)CH[(CH ₂) ₂ N(CH ₂) ₂]CN 4-(C ₆ H ₅ (CH ₂) ₂) ₂ C ₆ H ₄ CH ₂ CN	Cl(CH ₂) ₂ Br <i>i</i> -C ₃ H ₇ Br CH ₂ =CHCH ₂ Br ^d	" " "
		Cl(CH ₂) ₂ Br	"
		"	"
		"	"
		Cl(CH ₂) ₄ Cl ^e	"

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

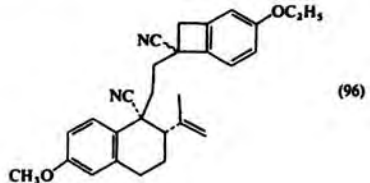

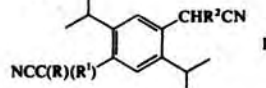
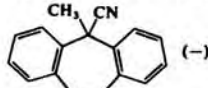
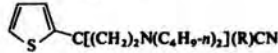
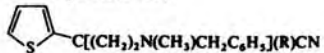
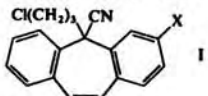
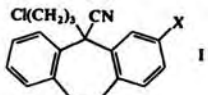
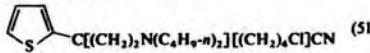
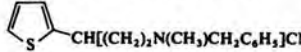
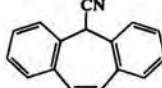
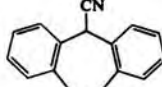
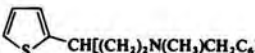
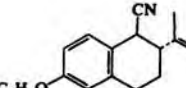
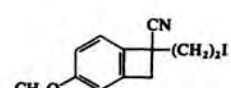
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Ether	1-C ₁₀ H ₇ C(CH ₂ CH=CH ₂)[(CH ₂) ₅ CH=CH ₂]CN (67)	664
NH ₃	 (96)	809
Et ₂ O	C ₆ H ₅  (58)	38
	 I	
THF	I, R = CH ₃ , R ¹ = R ² = H (-)	810
"	I, R = R ¹ = CH ₃ , R ² = H (-)	810
"	I, R = R ¹ = R ² = CH ₃ (-)	810
Et ₂ O	4-[C ₆ H ₅ (CH ₂) ₂] ₂ C ₆ H ₄ CH(CH ₂)CN (90)	775
"	4-[C ₆ H ₅ (CH ₂) ₂] ₂ C ₆ H ₄ CH(C ₂ H ₅)CN (84)	759
C ₆ H ₆ , toluene	 (-)	811
-	 C[(CH ₂) ₂ N(C ₄ H _{9-n}) ₂](R)CN	567
	R = CH ₂ CH=CH ₂ (84)	
	R = CH ₂ C≡CH (65)	
-	 C[(CH ₂) ₂ N(CH ₃)CH ₂ C ₆ H ₅](R)CN	568
	R = CH ₂ CH=CH ₂ (71)	
	R = C ₂ H ₅ - <i>i</i> (79)	
C ₆ H ₆	C ₆ H ₅ (CH ₂) ₂ C(C ₆ H ₅)[(CH ₂) ₂ Cl]CN (-)	721
Et ₂ O	2-C ₁₀ H ₇ C[(CH ₂) ₂ N(CH ₂) ₂](C ₃ H ₇ - <i>i</i>)CN (-)	621
"	4-[C ₆ H ₅ (CH ₂) ₂] ₂ C ₆ H ₄ CH(CH ₂ CH=CH ₂)CN (89)	775
	 I	
-	I, X = H (-)	812
-	I, X = Cl (-)	812
	 I	
-	I, X = H (-)	812
-	I, X = F (-)	812
-	I, X = Cl (-)	812
-	 C[(CH ₂) ₂ N(C ₄ H _{9-n}) ₂][(CH ₂) ₄ Cl]CN (51)	567

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₄ (Contd.)	4-[C ₆ H ₄ (CH ₂) ₂]C ₆ H ₄ CH ₂ CN (4-CH ₃ C ₆ H ₄) ₂ CHCN (4-CH ₃ OC ₆ H ₄) ₂ CHCN	<i>n</i> -C ₄ H ₉ Br ^f BrCH ₂ CO ₂ C ₂ H ₅ "	NaNH ₂ " "
	4-Isobutyl-1-naphthylacetonitrile	(CH ₃) ₂ N(CH ₂) ₂ Cl	"
	3-Methyl-2-(1-naphthyl)valeronitrile	"	"
		<i>n</i> -C ₄ H ₉ Br ^f	"
		BrCH ₂ CO ₂ C ₂ H ₅	NaOC ₂ H ₅
		XCH ₂ CO ₂ C ₂ H ₅	
	C ₆ H ₅ CH(C ₆ H _{11-n})CN C ₆ H ₅ (CH ₂) ₂ CH(C ₆ H ₅)CN 3-Methyl-2-(1-naphthyl)valeronitrile	ClCH ₂ CH(CH ₃)CH ₂ Br CH ₂ CHBrCO ₂ C ₂ H ₅ Br(CH ₂) ₂ CO ₂ C ₂ H ₅ (C ₂ H ₅ O) ₂ CHCH ₂ Br " (CH ₃) ₂ NCH ₂ CH(CH ₃)Cl	NaH NaOC ₂ H ₅ NaNH ₂ NaOC ₂ H ₅ " NaNH ₂ " "
		4-(2-Chloroethyl)morpholine	"
		1-(2-Chloroethyl)piperidine	"
		C ₆ H ₅ CH ₂ Cl ^f	"
	(4-CH ₃ C ₆ H ₄) ₂ CHCN 4-Ethyl-2-phenylheptanenitrile	C ₆ H ₅ O(CH ₂) ₂ Br [(C ₂ H ₅) ₂ NCH ₂] ₂ CHCl	LiN(C ₂ H ₅) ₂ NaNH ₂
	C ₆ H ₅ (CH ₂) ₂ CH(C ₆ H ₅)CN	<i>N</i> -(3-Bromopropyl)phthalimide	"
	2-(1-Naphthyl)hexanenitrile 2-(1-Naphthyl)-4-hexanenitrile	CH ₂ =CH(CH ₂) ₆ Cl "	" "
			" "
C ₁₇	(1-C ₁₀ H ₇)CH[(CH ₂) ₂ N(CH ₃) ₂]CN 5-Dimethylamino-2-(1-naphthyl)valeronitrile	C ₂ H ₅ Br ^f i-C ₃ H ₇ Br	" "

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

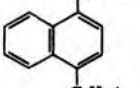
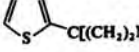
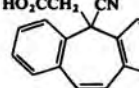
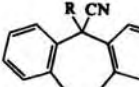
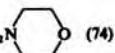
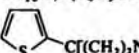
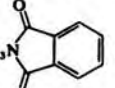

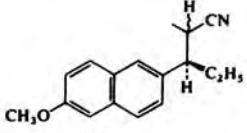
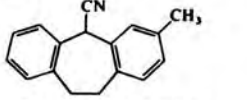
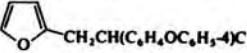

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₂ O Et ₂ O, DMF C ₆ H ₆	4-[C ₆ H ₄ (CH ₂) ₂]C ₆ H ₄ CH(C ₆ H _{9-n})CN (78) (4-CH ₃ C ₆ H ₄) ₂ C(CH ₂ CO ₂ C ₂ H ₅)CN (-) (4-CH ₃ OC ₆ H ₄) ₂ C(CH ₂ CO ₂ C ₂ H ₅)CN (-) CH[(CH ₂) ₂ N(CH ₃) ₂]CN	775 813 814
"	 (65)	815
"	1-C ₁₀ H ₇ C(C ₆ H _{9-sec})[(CH ₂) ₂ N(CH ₃) ₂]CN (92)	740
-	 Cl[(CH ₂) ₂ N(CH ₃) ₂](C ₆ H _{9-n})CN (76)	568
C ₂ H ₅ OH	HO ₂ CCH ₂ CN  (10) ^b	816
	 I	
Toluene C ₂ H ₅ OH -	I, X = Cl, R = CH ₂ CO ₂ C ₂ H ₅ (-) I, X = Br, R = CH ₂ CO ₂ H (91) ^b I, R = CH ₂ CH(CH ₃)CH ₂ Cl (-)	817 816 812
C ₂ H ₅ OH "	I, R = CH(CH ₃)CO ₂ C ₂ H ₅ (21) ^b I, R = (CH ₂) ₂ CO ₂ C ₂ H ₅ (55) ^b	816 816
Et ₂ O "	C ₆ H ₅ C(C ₆ H _{11-n})[CH ₂ CH(OC ₂ H ₅) ₂]CN (80) C ₆ H ₅ (CH ₂) ₂ C(C ₆ H ₅)[CH ₂ CH(OC ₂ H ₅) ₂]CN (85)	637,638 637,638
C ₆ H ₆	1-C ₁₀ H ₇ C(C ₆ H _{9-sec})[CH(CH ₃)CH ₂ N(CH ₃) ₂]CN (90)	740
"	1-C ₁₀ H ₇ C(C ₆ H _{9-sec})(CN)(CH ₂) ₂ N  (74)	740
"	1-C ₁₀ H ₇ C(C ₆ H _{9-sec})[(CH ₂) ₂ N(CH ₂) ₂]CN (87)	740
-	 Cl[(CH ₂) ₂ N(CH ₃) ₂](CH ₂) ₂ C ₆ H ₅]CN (73)	568
C ₆ H ₆ Toluene	(4-CH ₃ C ₆ H ₄) ₂ C[(CH ₂) ₂ OC ₂ H ₅]CN (88) C ₆ H ₅ C[CH ₂ CH(C ₂ H ₅)C ₂ H _{4-n}][CH(CH ₂ N(C ₂ H ₅) ₂)]CN (-)	562 665
C ₆ H ₆ , DMF	C ₆ H ₅ (CH ₂) ₂ C(C ₆ H ₅)(CN)(CH ₂) ₂ N  (72)	643,716
Et ₂ O "	1-C ₁₀ H ₇ C(C ₆ H _{9-n})[(CH ₂) ₂ CH=CH ₂]CN (70) 1-C ₁₀ H ₇ C(CH ₂ CH=CH ₂)[(CH ₂) ₂ CH=CH ₂]CN (61)	664 664
NH ₃	 (86)	809
C ₆ H ₆ "	1-C ₁₀ H ₇ C(C ₂ H ₅)[(CH ₂) ₂ N(CH ₃) ₂]CN (83) 1-C ₁₀ H ₇ C(C ₂ H ₅ - <i>o</i>)[(CH ₂) ₂ N(CH ₃) ₂]CN (90)	741 741

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₇ (Contd.)		CH ₂ =CHCH ₂ Br	NaC(C ₆ H ₅) ₃
		Cl(CH ₂) ₃ Br	NaNH ₂
	<i>n</i> -C ₄ H ₉ C(C ₂ H ₅) ₂ CH(R)CN	R'Br	"
	5-(Dimethylamino)-2-(1-naphthyl)valeronitrile	(CH ₃) ₂ N(CH ₂) ₃ Cl	"
	4-CH ₃ OC ₆ H ₄ CH ₂ CH(C ₆ H ₄ OCH ₃ -4)CN	(C ₂ H ₅) ₂ N(CH ₂) ₂ Cl	"
	4-((C ₂ H ₅) ₂ NCH ₂ CH ₂ O)-C ₆ H ₄ CH(C ₆ H ₄ CH ₃ -4)CN	C ₆ H ₅ CH ₂ Cl	"
C ₁₈	1-C ₁₀ H ₇ CH(C ₆ H ₅)CN	CH ₃ I' CH ₂ Br ₂ ' C ₂ H ₅ Br' Br(CH ₂) ₂ Br Br(CH ₂) ₂ CO ₂ H'	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl " " 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl "
	6-(Dimethylamino)-2-(1-naphthyl)hexanenitrile	<i>i</i> -C ₃ H ₇ Br	NaNH ₂
	1-C ₁₀ H ₇ CH(C ₆ H ₅)CN	"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		CH ₂ =CHCH ₂ Br' <i>n</i> -C ₄ H ₉ Br' Br(CH ₂) ₄ Br (C ₂ H ₅) ₂ N(CH ₂) ₂ Cl' C ₆ H ₅ CH ₂ Cl' 1-(2-Chloroethyl)piperidine' 1-(3-Chloropropyl)piperidine' (C ₆ H ₅) ₂ CHCl'	" " " " " " " " "
C ₁₉	1-C ₁₀ H ₇ CH(CH ₂ C ₆ H ₅)CN	CH ₃ I	"
	1-C ₁₀ H ₇ CH[(CH ₂) ₃ N(C ₂ H ₅) ₂]CN	<i>i</i> -C ₃ H ₇ Br	NaNH ₂
	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHCH(C ₆ H ₅)CN	"	"
	1-C ₁₀ H ₇ CH[(CH ₂) ₃ N(C ₂ H ₅) ₂]CN	"	"
	5-(1-Morpholino)-2-(1-naphthyl)valeronitrile	"	"
	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHCH(C ₆ H ₅)CN	<i>i</i> -C ₄ H ₉ Br	"
		(CH ₃) ₂ N(CH ₂) ₂ Cl	KNH ₂
	3-Cyclohexyl-3-(2-furyl)-2-phenylpropionitrile	"	"
	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHCH(C ₆ H ₅)CN		NaNH ₂
	1-C ₁₀ H ₇ CH[(CH ₂) ₃ N(C ₂ H ₅) ₂]CN	(CH ₂) ₃ N(CH ₂) ₂ Cl	"
	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHCH(C ₆ H ₅)CN	<i>n</i> -C ₈ H ₁₇ Br C ₆ H ₅ CH ₂ Cl	" "

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

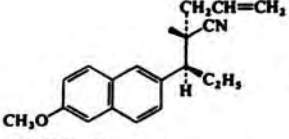
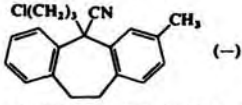


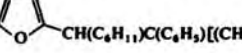
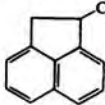
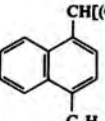
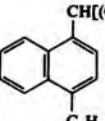
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	 (100)	818
—	 (—)	812
Et ₂ O " " THF C ₆ H ₆	<i>n</i> -C ₄ H ₉ C(C ₂ H ₅) ₂ C(R)(R')CN I, <i>n</i> -C ₄ H ₉ C(C ₂ H ₅) ₂ C(R)=C=N-R' II R = C ₆ H ₅ - <i>n</i> , R' = C ₆ H ₅ - <i>n</i> I (38), II (44) R = C ₆ H ₅ - <i>n</i> , R' = C ₆ H ₅ - <i>i</i> I (14), II (33) R = C ₆ H ₅ - <i>i</i> , R' = C ₆ H ₅ - <i>i</i> I (6), II (28) R = C ₆ H ₅ - <i>n</i> , R' = C ₆ H ₅ - <i>n</i> I (27), II (39) 1-C ₁₀ H ₇ C[(CH ₂) ₃ N(CH ₂) ₂] ₂ CN (86)	256 256 256 256 741
Toluene NH ₃ , Et ₂ O	4-CH ₃ OC ₆ H ₄ CH ₂ C(C ₆ H ₄ OCH ₃ -4)[(CH ₂) ₃ N(C ₂ H ₅) ₂]CN (—) 4-[(C ₂ H ₅) ₂ N(CH ₂) ₂ O]C ₆ H ₄ C(C ₆ H ₄ CH ₃ -4)(CH ₂ C ₆ H ₅)CN (—)	819 820
—	1-C ₁₀ H ₇ C(C ₆ H ₅)(CH ₃)CN (95) 1-C ₁₀ H ₇ C(C ₆ H ₅)(CH ₂ Br)CN (85) 1-C ₁₀ H ₇ C(C ₆ H ₅)(C ₂ H ₅)CN (91) 1-C ₁₀ H ₇ C(C ₆ H ₅)[(CH ₂) ₂ Br]CN (88) 1-C ₁₀ H ₇ C(C ₆ H ₅)[(CH ₂) ₂ CO ₂ H]CN (—) 1-C ₁₀ H ₇ C[(CH ₂) ₄ N(CH ₂) ₂](C ₆ H ₅ - <i>i</i>)CN (—)	97 97 97 97 97 629
—	1-C ₁₀ H ₇ C(C ₆ H ₅)(C ₂ H ₅ - <i>i</i>)CN (50) 1-C ₁₀ H ₇ C(C ₆ H ₅)(CH ₂ CH=CH ₂)CN (99) 1-C ₁₀ H ₇ C(C ₆ H ₅)(C ₆ H ₅ - <i>n</i>)CN (88) 1-C ₁₀ H ₇ C(C ₆ H ₅)[(CH ₂) ₄ Br]CN (92) 1-C ₁₀ H ₇ C(C ₆ H ₅)[(CH ₂) ₂ N(C ₂ H ₅) ₂]CN (66) 1-C ₁₀ H ₇ C(C ₆ H ₅)(CH ₂ C ₆ H ₅)CN (99) 1-C ₁₀ H ₇ C(C ₆ H ₅)[(CH ₂) ₂ N(CH ₂) ₂]CN (42) 1-C ₁₀ H ₇ C(C ₆ H ₅)[(CH ₂) ₃ N(CH ₂) ₂]CN (99) 1-C ₁₀ H ₇ C(C ₆ H ₅)[CH(C ₆ H ₅) ₂]CN (50) 1-C ₁₀ H ₇ C(CH ₂ C ₆ H ₅)(CH ₃)CN (69) " (100)	97 97 97 97 97 97 97 97 97 97 747
Toluene C ₆ H ₆ Toluene C ₆ H ₆	1-C ₁₀ H ₇ C[(CH ₂) ₃ N(C ₂ H ₅) ₂](C ₆ H ₅ - <i>i</i>)CN (86) [(C ₂ H ₅) ₂ NCH ₂] ₂ CHC(C ₆ H ₅)(C ₆ H ₅)CN (—) 1-C ₁₀ H ₇ C[(CH ₂) ₃ N(CH ₂) ₂](C ₆ H ₅ - <i>i</i>)CN (74)	741 611 741
—	1-C ₁₀ H ₇ C(C ₂ H ₅ - <i>i</i>)(CN)(CH ₂) ₂ N  (58)	741
Toluene	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHC(C ₆ H ₅)(C ₆ H ₅ - <i>i</i>)CN (—)	611
—	 -CH ₂ C(C ₆ H ₄ OC ₆ H ₄ -4)[(CH ₂) ₃ N(CH ₂) ₂]CN	635
—	 -CH(C ₆ H ₁₁)C(C ₆ H ₅)[(CH ₂) ₃ N(CH ₂) ₂]CN (—)	753
—	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHC(C ₆ H ₅)(C ₆ H ₅)CN (—)	611
C ₆ H ₆ Toluene "	1-C ₁₀ H ₇ C[(CH ₂) ₃ N(C ₂ H ₅) ₂][(CH ₂) ₃ N(CH ₂) ₂]CN (—) [(C ₂ H ₅) ₂ NCH ₂] ₂ CHC(C ₆ H ₅)(C ₆ H ₁₃ - <i>n</i>)(CN) (—) [(C ₂ H ₅) ₂ NCH ₂] ₂ CHC(C ₆ H ₅)(CH ₂ C ₆ H ₅)CN (—)	741 611 611

TABLE I. ALKYLATION OF NITRILE-STABILIZED CARBANIONS WITH

No. of C Atoms	Nucleophile	Electrophile	Base	
C ₁₉ (Contd.)	C ₆ H ₅ CH(CN)CH[CH ₂ N(C ₂ H ₅) ₂]	C ₆ H ₅ CH ₂ Cl	NaNH ₂	
	3-Cyclohexyl-3-(2-furyl)-2-phenylpropionitrile	1-(2-Chloroethyl)piperidine	KNH ₂	
	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHCH(C ₆ H ₅)CN	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHCl	NaNH ₂	
	4-C ₆ H ₁₁ C ₆ H ₄ CH(C ₃ H ₇ - <i>i</i>)CN	"	"	
C ₂₀	1-C ₁₀ H ₇ CH[(CH ₂) ₃ N(CH ₂) ₃]CN	<i>i</i> -C ₃ H ₇ Br	"	
	4-C ₆ H ₁₁ C ₆ H ₄ CH(C ₆ H ₁₁)CN	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHCl	"	
C ₂₁		1-Chloroacenaphthene	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
	(C ₆ H ₅) ₂ CHCH(C ₆ H ₅)CN	<i>n</i> -C ₄ H ₉ Br	KNH ₂ (1 eq)	
C ₂₂	ArCH(C ₆ H ₄ CH ₃ -4)CN	Ar'CH ₂ Cl	" (2 eq)	
	(C ₆ H ₅) ₂ CHCH(C ₆ H ₅)CN	C ₆ H ₅ CH ₂ Cl	NaNH ₂	"
			"	"
			"	"
			"	"
			"	"
			"	"
			"	"
			"	"
			"	"
			"	"
		C ₆ H ₅ CH ₂ Cl	KNH ₂	"
"			"	
4-C ₆ H ₅ CH ₂ OC ₆ H ₄ CH(C ₆ H ₄ CH ₃ -4)CN	C ₆ H ₅ CH ₂ Cl	KNH ₂	"	
		4-C ₆ H ₅ C ₆ H ₄ CH[(CH ₂) ₂ N(C ₃ H ₇ - <i>i</i>) ₂]CN	"	
		3,4-(C ₆ H ₅ CH ₂ O) ₂ C ₆ H ₃ CH ₂ CN	"	
		(C ₆ H ₅) ₂ P=C(CO ₂ CH ₃)CH ₂ CN	"	
C ₂₂		<i>i</i> -C ₃ H ₇ Br	NaNH ₂	
		3-ClC ₆ H ₄ CH ₂ Cl	KNH ₂	
		(<i>i</i> -C ₃ H ₇) ₂ N(CH ₂) ₂ Cl	NaNH ₂	
		3,4,5-(CH ₂ O) ₃ C ₆ H ₂ CH ₂ Cl	LDA	
C ₂	Ⓟ-CH ₂ CN	ClCH ₂ CN	50% aq NaOH, Adogen 464	

^a The initial product was treated with (CH₃)₂SiCl.

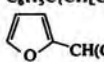
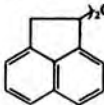
^b The initial product was hydrolyzed.

^c The precise leaving group in the alkylating agent was unspecified.

^d The product was isolated as the corresponding amide after treatment with aqueous acid.

^e The alcohol was oxidized in a Guerbet reaction to an aldehyde, which condensed with the nitrile starting material. Subsequently, the unsaturated nitrile was reduced to the observed product.

ALKYL HALIDES, ALKYL SULFONATES, EPOXIDES, AND AZIRIDINES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Toluene	C ₆ H ₅ C[CH[CH ₂ N(C ₂ H ₅) ₂](CH ₂ C ₆ H ₅)CN (45)	665
"	 CH(C ₆ H ₁₁)C(C ₆ H ₅)[(CH ₂) ₂ N(CH ₂) ₃]CN (-)	753
"	[(C ₂ H ₅) ₂ NCH ₂] ₂ CHC(C ₆ H ₅)[CH[CH ₂ N(C ₂ H ₅) ₂] ₂]CN (-)	611
"	4-C ₆ H ₁₁ C ₆ H ₄ C(C ₃ H ₇ - <i>i</i>)CH[CH ₂ N(C ₂ H ₅) ₂] ₂]CN (-)	665
C ₆ H ₆	1-C ₁₀ H ₇ Cl[(CH ₂) ₃ N(CH ₂) ₃](C ₃ H ₇ - <i>i</i>)CN (73)	741
Toluene	4-C ₆ H ₁₁ C ₆ H ₄ C(C ₆ H ₁₁)[CH[CH ₂ N(C ₂ H ₅) ₂] ₂]CN (-)	665
—	 C(C ₆ H ₅)CN (31)	81
NH ₃	(C ₆ H ₅) ₂ CHC(C ₆ H ₅)(C ₄ H ₉ - <i>n</i>)CN (85)	110
"	(C ₆ H ₅) ₂ C(C ₆ H ₅ - <i>n</i>)CH(C ₆ H ₅)CN (95)	110
"	ArC(C ₆ H ₄ CH ₃ -4)(CH ₂ Ar')CN 1	
"	Ar = C ₆ H ₄ [O(CH ₂) ₂ N(C ₂ H ₅) ₂]-4	
NH ₃ or toluene	1, Ar' = C ₆ H ₄ Cl-4 (53)	821
NH ₃	= C ₆ H ₅ (61)	821
Toluene	= C ₆ H ₄ Cl-2 (46)	821
"	= C ₆ H ₄ Cl-3 (12)	821
NH ₃	= C ₆ H ₃ Cl ₂ -3,4 (83)	821
"	= C ₆ H ₂ Cl ₃ -2,4 (73)	821
"	= C ₆ H ₄ NO ₂ -4 (58)	821
"	= C ₆ H ₄ NO ₂ -3 (57)	821
"	= C ₆ H ₄ F-4 (79)	821
Toluene	= C ₆ H ₁₁ (39)	821
NH ₃	= (C ₆ H ₅ N-4) (-)	821
"	= C ₆ H ₄ OCH ₃ -4 (93)	821
"	= C ₆ H ₄ CF ₃ -4 (74)	821
"	= C ₆ H ₄ CH ₃ -4 (74)	821
NH ₃	(C ₆ H ₅) ₂ C(CH ₂ C ₆ H ₅)CH(C ₆ H ₅)CN (80)	109,108
"	(C ₆ H ₅) ₂ CHC(C ₆ H ₅)(CH ₂ C ₆ H ₅)CN (-)	108
NH ₃ , Et ₂ O	((C ₆ H ₅) ₂ CH) ₂ C(C ₆ H ₅)CN (33)	161
NH ₃	" (63)	110
C ₆ H ₆	1-(4- <i>i</i> -C ₆ H ₉)C ₁₀ H ₆ C(C ₃ H ₇ - <i>i</i>)[(CH ₂) ₃ N(C ₃ H ₇ - <i>i</i>) ₂]CN	815
—	4-C ₆ H ₅ CH ₂ OC ₆ H ₄ C(C ₆ H ₄ CH ₃ -4)(CH ₂ C ₆ H ₄ Cl-3)CN (-)	820
Toluene	4-C ₆ H ₅ C ₆ H ₄ C[(CH ₂) ₂ N(C ₃ H ₇ - <i>i</i>) ₂] ₂]CN (-)	803
THF	3,4-(C ₆ H ₅ CH ₂ O) ₂ C ₆ H ₃ CH(CH ₂ C ₆ H ₅ (OCH ₂) ₂ -3,4,5)CN (45)	822
THF	(C ₆ H ₅) ₂ P=C(CO ₂ CH ₃)CH(C ₁₀ H ₂₁ - <i>n</i>)CN (94)	823
1,2-Cl ₂ C ₆ H ₄	Ⓟ-CH(CH ₂ CN)CN (88)	824

^f The yields were determined by vapor-phase chromatography.

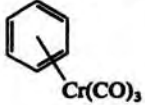
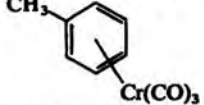
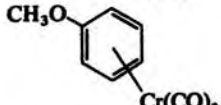
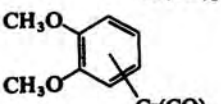
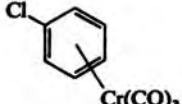
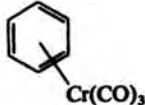
^g The initial product was converted to a carboxylic ester.

^h The alkylation of the dianion of the γ -ketonitrile with one equivalent of alkylating agent was followed by the spontaneous elimination of HCN. Alternatively, the alkylated γ -ketonitrile was treated with NaNH₂ in C₆H₆ to effect elimination of HCN.

ⁱ The product was isolated as a mixture of the hydroxynitrile and cyclic iminoester.

^j The product was isolated as the cyclic ammonium halide.

TABLE II. ARYLATION OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₂	CH ₃ CN	C ₆ H ₅ X	KNH ₂ , K
		C ₆ H ₅ Cl [C ₆ H ₅ N(CH ₃) ₂]I	KNH ₂ KNH ₂ , K
			LDA
		"	"
		C ₆ H ₅ OP(O)(OC ₂ H ₅) ₂	KNH ₂ , K
			LDA
			"
			"
		C ₆ H ₅ I C ₆ H ₅ Br	KNH ₂ , K NaNH ₂
			LDA
"	"		
	"		
"	"		

C₄ *n*-C₃H₇CN
 i-C₃H₇CN

STABILIZED CARBANIONS

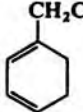
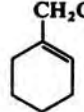
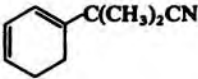
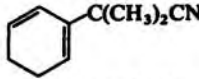
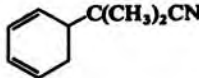
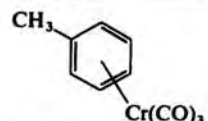
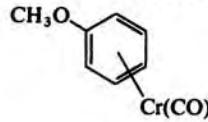
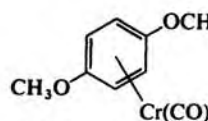
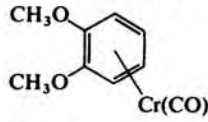
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	C ₆ H ₅ CH ₂ CN (2-31) X = F, Cl, Br, I	145
NH ₃	C ₆ H ₅ CH ₂ CN (—), (C ₆ H ₅) ₂ CHCN (—)	142
—	C ₆ H ₅ CH ₂ CN (5)	145
THF, 0°	C ₆ H ₅ CH ₂ CN (68) ^a	146
THF, -30°	 (60) ^b +  (10) ^b	146,283
—	C ₆ H ₅ CH ₂ CN (3)	145
THF, HMPA	2-CH ₃ C ₆ H ₄ CH ₂ CN (35), ^a 3-CH ₃ C ₆ H ₄ CH ₂ CN (63), ^a 4-CH ₃ C ₆ H ₄ CH ₂ CN (2), ^a	283,146
THF	2-CH ₃ OC ₆ H ₄ CH ₂ CN (3), ^a 3-CH ₃ OC ₆ H ₄ CH ₂ CN (97) ^a	283,146
THF, HMPA	2,3-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN (48) ^a	283,146
—	C ₆ H ₅ CH(C ₂ H ₅)CN (29), C ₆ H ₅ CH ₂ CH ₂ CH ₃ (6)	145
NH ₃	C ₆ H ₅ C(CH ₃) ₂ CN I (23)	141
THF, 15-20 hr, 25°	" (85) ^a	146
THF, 15 min, 0°	2-ClC ₆ H ₄ C(CH ₃) ₂ CN (2), ^a 3-ClC ₆ H ₄ C(CH ₃) ₂ CN (56), ^a I (19) ^a	146
"	I (94) ^a	146
THF	 (80) ^b +  (5) ^b +  (5) ^b	146

TABLE II. ARYLATION OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₄ (Contd.)	<i>i</i> -C ₃ H ₇ CN		LDA
			"
		"	"
		"	"
			LDA
			"
C ₅	<i>i</i> -C ₄ H ₉ CN	C ₆ H ₅ Cl	KNH ₂ , K
C ₆	Pyrazineacetonitrile	C ₆ H ₅ Br	NaNH ₂
C ₈	2-ClC ₆ H ₄ CH ₂ CN C ₆ H ₅ CH ₂ CN	2-Chloropyrimidine	NaH
		2-Chloropyrazine	NaNH ₂
	4-ClC ₆ H ₄ CH ₂ CN	2-Bromopyridine	"
		3-Bromopyridine	"
		4-Bromopyridine	"
XC ₆ H ₄ CH ₂ CN	4-YC ₆ H ₄ NO ₂		"
			"
			KOH
			"
			"

STABILIZED CARBANIONS (Continued)

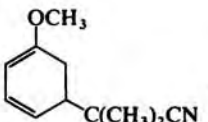
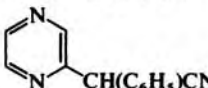
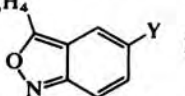
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF, HMPA	2-CH ₃ C ₆ H ₄ C(CH ₃) ₂ CN (1-2), ^a 3-CH ₃ C ₆ H ₄ C(CH ₃) ₂ CN (96-97), ^a 4-CH ₃ C ₆ H ₄ C(CH ₃) ₂ CN (2) ^a	283,146
THF	2-CH ₃ OC ₆ H ₄ C(CH ₃) ₂ CN (3), ^a 3-CH ₃ OC ₆ H ₄ C(CH ₃) ₂ CN (97) ^a	283,146,285
"	 (98) ^c	285
"	3-HOC ₆ H ₄ C(CH ₃) ₂ CN (50) ^b	285
"	C ₆ H ₅ C(CH ₃) ₂ CN (55) ^d	285
THF, HMPA	2,5-(CH ₃ O) ₂ C ₆ H ₃ C(CH ₃) ₂ CN (92) ^a	283,146
"	2,3-(CH ₃ O) ₂ C ₆ H ₃ C(CH ₃) ₂ CN (85), ^a 3,4-(CH ₃ O) ₂ C ₆ H ₃ C(CH ₃) ₂ CN (13) ^a	283,146
—	C ₆ H ₅ CH(C ₃ H ₇ - <i>i</i>)CN (19), C ₆ H ₅ CH ₂ CH(CH ₃) ₂ (37)	145
NH ₃ , dioxane	 (—)	272
THF	2-ClC ₆ H ₄ CH(C ₄ H ₉ N ₂)CN (28)	827
Toluene	C ₆ H ₅ CH(C ₄ H ₉ N ₂)CN (80)	731
"	C ₆ H ₅ CH(C ₅ H ₄ N-2)CN (—)	828
"	C ₆ H ₅ CH(C ₅ H ₄ N-3)CN (—)	828
"	C ₆ H ₅ CH(C ₅ H ₄ N-4)CN (—)	828
"	4-ClC ₆ H ₄ CH(C ₅ H ₄ N-2)CN (—)	828
	4-XC ₆ H ₄  I,	
	4-XC ₆ H ₄ CH(C ₆ H ₄ NO ₂ -4)CN II	
CH ₃ OH	I X = H, Y = Cl (46)	154
"	I X = H, Y = Br (79)	154
"	I X = Y = Cl (46)	154
"	I X = Cl, Y = Br (48)	154
Py	II X = H, Y = Cl (68)	154
"	II X = H, Y = Br (76)	154
"	II X = H, Y = OCH ₃ (45)	154

TABLE II. ARYLATION OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base	
C ₈ (Contd.)	XC ₆ H ₄ CH ₂ CN	4-YC ₆ H ₄ NO ₂	KOH	
		"	"	
		"	"	
		"	"	
		"	"	
	C ₆ H ₅ CH ₂ CN	3-O ₂ NC ₆ H ₄ CO ₂ H	"	
		3,4-(O ₂ N)ClC ₆ H ₃ CO ₂ H	"	
		C ₆ H ₅ I	C ₁₀ H ₈ Na	
	4-XC ₆ H ₄ CH ₂ CN	YC ₆ H ₄ NO ₂		KOH
				"
				"
				"
"				
"				
"				
"				
"				
"				
"				

STABILIZED CARBANIONS (Continued)

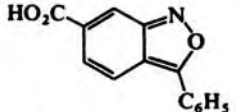
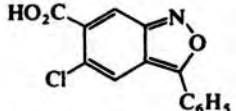
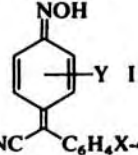
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
CH ₃ OH	II X = H, Y = OCH ₃ (15)	154
Py	II X = Y = Cl (86)	154
"	II X = Cl, Y = Br (87)	154
"	II X = Cl, Y = OCH ₃ (55)	154
CH ₃ OH	II X = Cl, Y = OCH ₃ (18)	154
Py	II X = Y = OCH ₃ (34)	154
CH ₃ OH	II X = Y = OCH ₃ (9)	154
"	 (88)	156
"	 (59)	156
THF	(C ₆ H ₅) ₂ CHCN (11)	198
"		
CH ₃ OH	I X = H, Y = H (77)	158
"	I X = H, Y = Cl-2 (92)	157
"	I X = H, Y = Cl-3 (53)	157
"	I X = H, Y = CH ₃ -2 (72)	157
"	I X = H, Y = CH ₃ -3 (76)	157
"	I X = H, Y = OCH ₃ -2 (87)	157
"	I X = H, Y = OCH ₃ -3 (25)	157
"	I X = H, Y = CH ₃ -2, Cl-3 (82)	157
"	I X = H, Y = Cl ₂ -2,3 (53)	157
"	I X = H, Y = Cl ₂ -2,5 (93)	157
"	I X = H, Y = (OCH ₃) ₂ -2,5 (88)	157
"	I X = H, Y = (CH ₃) ₂ -2,5 (53)	157
"	I X = H, Y = OCH ₃ -2, Cl-5 (82)	157
"	I X = H, Y = CH ₃ -2, Cl-5 (92)	157
"	I X = H, Y = Cl-2, CH ₃ -5 (77)	157
"	I X = Cl, Y = H (77)	158
"	I X = Cl, Y = Cl-2 (100)	157
"	I X = Cl, Y = Cl-3 (100)	157
"	I X = Cl, Y = CH ₃ -2 (60)	157
"	I X = Cl, Y = CH ₃ -3 (33)	157
"	I X = Cl, Y = OCH ₃ -2 (80)	157
"	I X = Cl, Y = OCH ₃ -3 (89)	157
"	I X = Cl, Y = CH ₃ -2, Cl-3 (80)	157
"	I X = Cl, Y = Cl ₂ -2,3 (92)	157
"	I X = Cl, Y = Cl ₂ -3,5 (94)	157
"	I X = Cl, Y = (OCH ₃) ₂ -3,5 (80)	157

TABLE II. ARYLATION OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₈ (Contd.)	4-XC ₆ H ₄ CH ₂ CN	YC ₆ H ₄ NO ₂	KOH
			"
C ₆ H ₅ CH ₂ CN	Methyl 6-chloronicotinate	Ethyl 6-chloronicotinate	NaNH ₂
			"
4-XC ₆ H ₄ CH ₂ CN	C ₁₀ H ₇ NO ₂ -1	KOH	"
			"
C ₆ H ₅ CH ₂ CN	9-Fluorobenzanthrone	"	"
C ₆ H ₅ ¹³ CH ₂ CN	"	"	"
4-FC ₆ H ₄ CH ₂ CN	"	"	"
C ₉	4-CH ₃ C ₆ H ₄ CH ₂ CN	2-Chloropyrazine	NaNH ₂
			"
C ₉	4-CH ₃ OC ₆ H ₄ CH ₂ CN	YC ₆ H ₄ NO ₂	KOH
			"
			"
			"
			"
			"
			"
			"

STABILIZED CARBANIONS (Continued)

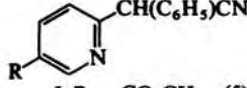
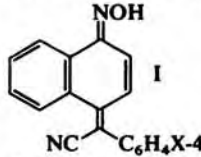
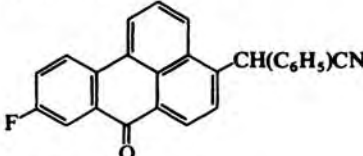
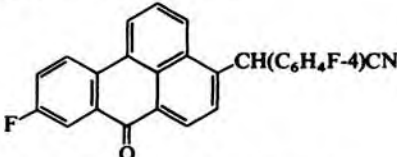
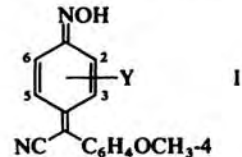
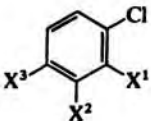
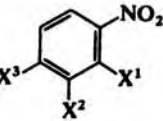
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
CH ₃ OH	I X = Cl, Y = (CH ₃) ₂ -3,5 (43)	157
"	I X = Cl, Y = OCH ₃ -2, Cl-5 (81)	157
"	I X = Cl, Y = CH ₃ -2, Cl-5 (87)	157
"	I X = Cl, Y = Cl-2, CH ₃ -5 (77)	157
C ₆ H ₆	 I	829
"	I, R = CO ₂ CH ₃ (5)	
"	I, R = CO ₂ C ₂ H ₅ (44)	829
CH ₃ OH	 I	157
"	I X = H (33)	157
"	I X = Cl (88)	157
<i>i</i> -C ₃ H ₇ OH	 I (55)*	830
"	I (with ¹³ C label) (82)*	831
"	 I (50)*	830
C ₆ H ₆	4-CH ₃ C ₆ H ₄ CH(C ₄ H ₃ N ₂)CN (62)	731
CH ₃ OH	 I	158
"	I Y = H (77)	157
"	I Y = CH ₃ -2, Cl-3 (80)	157
"	I Y = Cl ₂ -3,5 (91)	157
"	I Y = (OCH ₃) ₂ -3,5 (65)	157
"	I Y = (CH ₃) ₂ -3,5 (69)	157
"	I Y = OCH ₃ -2, Cl-5 (84)	157
"	I Y = CH ₃ -2, Cl-5 (88)	157
"	I Y = Cl-2, CH ₃ -5 (80)	157

TABLE II. ARYLATION OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₉ (Contd.)	4-CH ₃ OC ₆ H ₄ CH ₂ CN	1-Nitronaphthalene	KOH
	4-XC ₆ H ₄ CH ₂ CN	4-YC ₆ H ₄ NO ₂	"
	2-NCC ₆ H ₄ CH ₂ CN	XC ₆ H ₄ Br	"
	C ₆ H ₅ CH(CH ₃)CN		50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
			"
			50% aq NaOH, dibenzo-[18]-crown-6

STABILIZED CARBANIONS (Continued)

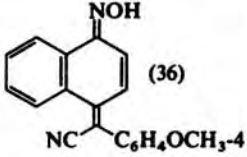
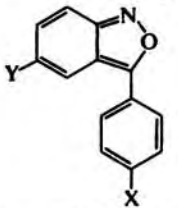
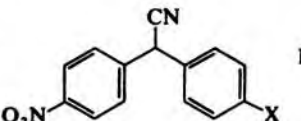
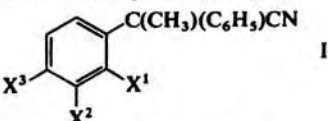
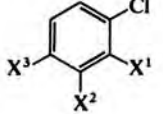
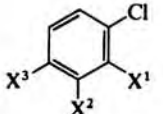
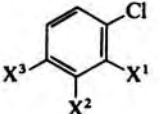
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
CH ₃ OH	 (36)	157
"	 I,	
"	 II	
"	I X = OCH ₃ , Y = Cl (49)	154
"	I X = OCH ₃ , Y = Br (69)	154
Py	II X = OCH ₃ , Y = Cl (65)	154
"	II X = OCH ₃ , Y = Br (65)	154
"	II X = Y = OCH ₃ (34)	154
CH ₃ OH	II X = Y = OCH ₃ (9)	154
"	XC ₆ H ₄ CH(C ₆ H ₄ CN-2)CN I	
Py	I X = NO ₂ -4 (69)	832
"	I X = NO ₂ -2 (-)	832
"	I X = OCH ₃ -3-NO ₂ -4 (63)	832
	 I	
"	I X ¹ = X ² = H, X ³ = NO ₂ (82)	82-85
"	I X ² = X ³ = H, X ¹ = NO ₂ (80)	83,82,84
"	I X ¹ = CO ₂ C ₄ H ₉ -t, X ² = H, X ³ = NO ₂ (83)	83,82,84
"	I X ¹ = CH ₃ , X ² = H, X ³ = NO ₂ (88)	83,82
"	I X ¹ = Cl, X ² = H, X ³ = NO ₂ (92)	86,82-84
"	I X ¹ = NO ₂ , X ² = H, X ³ = Cl (85)	86,83
"	I X ¹ = X ³ = NO ₂ , X ² = H (75)	86,83
"	I X ¹ = H, X ² = Cl, X ³ = NO ₂ (82)	83
"	I X ¹ = H, X ² = OCH ₃ , X ³ = NO ₂ (81)	83
"	I X ¹ = COC ₆ H ₅ , X ² = H, X ³ = NO ₂ (67)	87,83
"	I X ¹ = X ² = H, X ³ = COC ₆ H ₄ Cl-4 (75)	87,83
"	I X ¹ = X ² = H, X ³ = COC ₆ H ₄ Br-4 (69)	87,83
"	I X ¹ = X ² = H, X ³ = COC ₆ H ₄ OCH ₃ -4 (64)	87,83
"	I X ¹ = X ² = H, X ³ = COC ₆ H ₄ CH ₃ -4 (93)	87,83
"	I X ¹ = X ² = H, X ³ = COC ₆ H ₅ (82)	87,83
"	I X ¹ = X ² = H, X ³ = COC ₆ H ₅ (67)	527
"	I X ¹ = X ² = H, X ³ = NO ₂ (81)	527

TABLE II. ARYLATION OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base	
C ₉ (Contd.)	C ₆ H ₅ CH(CH ₃)CN	C ₆ H ₅ NO ₂	NaNH ₂ or NaOCH ₃	
C ₁₀	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN	2-Chloropyrazine	NaOH or NaOCH ₃ NaNH ₂	
	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN	2-Bromopyridine	"	
	C ₆ H ₅ CH(C ₂ H ₅)CN		50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	"
				"
				"
C ₆ H ₅ CH(C ₂ H ₅)CN		50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	"	
			"	
			"	
C ₁₁	3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CH ₂ CN	2-Chloropyridine	NaH	
	C ₆ H ₅ CH(C ₃ H _{7-n})CN		50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	

STABILIZED CARBANIONS (Continued)

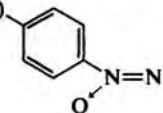
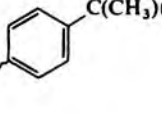
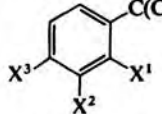
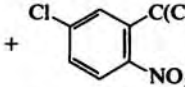
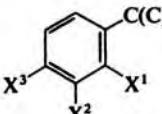
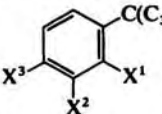
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NH ₃ or - THF, -30 to -60°	C ₆ H ₅ C(CH ₃)(C ₆ H ₄ NO ₂ -4)CN (15), C ₆ H ₅ C(CH ₃)(C ₆ H ₄ NH ₂ -4)CN (15), C ₆ H ₅ COCH ₃ I (30), C ₆ H ₅ C(CH ₃)(CN)-  -N=N-  II (30)	267
CH ₃ OH	I (30), II (60)	267
NH ₃ , ether, dioxane	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH(C ₄ H ₉ N ₂)CN (35)	731
Toluene	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH(C ₅ H ₄ N-2)CN (-)  I	828
-	I X ¹ = X ² = H, X ³ = Cl (95)	83
-	I X ¹ = NO ₂ , X ² = X ³ = H (95)	83
-	I X ¹ = Cl, X ² = H, X ³ = NO ₂ (61)	86,83
-	I X ¹ = NO ₂ , X ² = H, X ³ = Cl (75)	86,83
-	I X ¹ = X ³ = NO ₂ , X ² = H (61)	86,83
-	I X ¹ = H, X ² = Cl, X ³ = NO ₂ (78)	83
-	+  C(C ₂ H ₅)(C ₆ H ₅)CN (3)	
-	 I	
-	I X ¹ = COC ₆ H ₅ , X ² = H, X ³ = NO ₂ (90)	87,83
-	I X ¹ = X ² = H, X ³ = COC ₆ H ₄ Cl-4 (70)	87,83
-	I X ¹ = X ² = H, X ³ = COC ₆ H ₄ Br-4 (61)	87,83
-	I X ¹ = X ² = H, X ³ = COC ₆ H ₅ (89)	87,83
DMF	3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CH(C ₅ H ₄ N-2)CN (59, crude)	833
-	 I	
-	I X ¹ = X ² = H, X ³ = NO ₂ (74)	84,82,83

TABLE II. ARYLATION OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₁ (Contd.)	C ₆ H ₅ CH(C ₃ H _{7-i})CN		50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
		"	"
	C ₆ H ₅ CH(C ₃ H _{7-n})CN		"
			"
C ₆ H ₅ CH(C ₃ H _{7-i})CN		"	
	"	"	
C ₁₂	1-Naphthylacetonitrile	C ₆ H ₅ NO ₂	KOH
	C ₆ H ₅ CH[(CH ₂) ₂ N(CH ₃) ₂]CN	4-Chlorocinnoline	NaNH ₂
C ₁₃	C ₆ H ₅ CH[(CH ₂) ₃ N(CH ₃) ₂]CN	"	"
C ₁₄	(C ₆ H ₅) ₂ CHCN	2-Chloropyrazine	"
	4-ClC ₆ H ₄ CH(C ₆ H ₅)CN	"	"
	(C ₆ H ₅) ₂ CHCN		"

STABILIZED CARBANIONS (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	 II	
—	II X ¹ = X ² = H, X ³ = NO ₂ (62)	83
—	II X ¹ = Cl, X ² = H, X ³ = NO ₂ (30)	86,83
—	II X ¹ = X ³ = NO ₂ , X ² = H (20)	86,83
	 I	
—	I X ¹ = COC ₆ H ₅ , X ² = H, X ³ = NO ₂ (60)	83,87
—	I X ¹ = X ² = H, X ³ = COC ₆ H ₄ Cl-4 (78)	83,87
—	 II	83,87
—	II X ¹ = COC ₆ H ₅ , X ² = H, X ³ = NO ₂ (60)	83,87
CH ₃ OH	 (65)	158
C ₆ H ₆	 (87)	632
"	 (73)	632
Toluene	(C ₆ H ₅) ₂ C(C ₄ H ₃ N ₂)CN (46)	731
"	4-ClC ₆ H ₄ C(C ₆ H ₅)(C ₄ H ₃ N ₂)CN (57)	731
	 I	

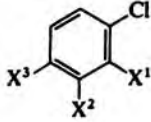
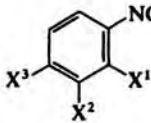

TABLE II. ARYLATION OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₄ (Contd.)	(C ₆ H ₅) ₂ CHCN		50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
			"
			"
			"
			NaOCH ₃
		2-Chloro-3-ethylpyrazine	NaNH ₂
		2-Chloro-5,6-dimethylpyrazine	"
		4-Chlorocinnoline	"
		"	"
C ₁₅	4-CH ₃ OC ₆ H ₄ CH(C ₆ H ₅)CN	2-Chloropyrazine	"
			50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
			"
			"
			"

STABILIZED CARBANIONS (Continued)

Reaction Conditions	Product(s) and Yield(s) (-)	Refs.
—	I X ¹ = X ² = H, X ³ = NO ₂ (71)	83,82,84
—	I X ¹ = NO ₂ , X ² = X ³ = H (88)	83
—	I X ¹ = Cl, X ² = H, X ³ = NO ₂ (90)	83,86
—	I X ¹ = NO ₂ , X ² = H, X ³ = Cl (93)	83
—	I X ¹ = X ³ = NO ₂ , X ² = H (91)	86,83
	(C ₆ H ₅) ₂ C=N(O)-	II
CH ₃ OH	II X ¹ = X ² = H (96)	83
"	II X ¹ = Cl, X ² = H (88-92)	83
"	II X ¹ = Br, X ² = H (87)	83
"	II X ¹ = OCH ₃ , X ² = H (66)	83
"	II X ¹ = H, X ² = OCH ₃ (91)	83
Toluene		731
"		731
C ₆ H ₆		632
"		632
Toluene		(48)
		I
—	I X ¹ = X ² = H, X ³ = NO ₂ (88)	84,82,83
—	I X ¹ = NO ₂ , X ² = X ³ = H (84)	83
—	I X ¹ = Cl, X ² = H, X ³ = NO ₂ (82)	86,83
—	I X ¹ = NO ₂ , X ² = H, X ³ = Cl (98)	86,83
—	I X ¹ = X ³ = NO ₂ , X ² = H (91)	84,83,86

TABLE II. ARYLATION OF NITRILE-

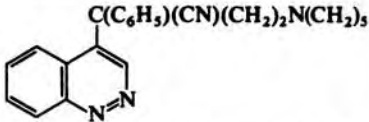
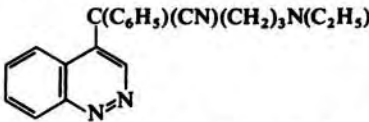
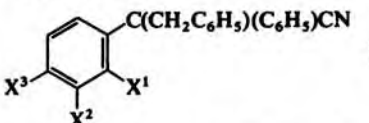
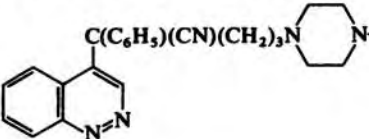
No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₅ (Contd.)	C ₆ H ₅ CH[(CH ₂) ₂ N(CH ₂) ₅]CN	4-Chlorocinnoline	NaNH ₂
	C ₆ H ₅ CH[(CH ₂) ₃ N(C ₂ H ₅) ₂]CN	"	"
	C ₆ H ₅ CH(CH ₂ C ₆ H ₅)CN		50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
			"
		"	"
		"	"
C ₁₆	C ₆ H ₅ CH(CN)(CH ₂) ₃ N 	4-Chlorocinnoline	NaNH ₂

^a The initial product was oxidized with iodine.

^b The initial product was quenched with CF₃CO₂H at low temperature and oxidized with iodine.

^c The initial product was quenched with CF₃CO₂H at low temperature and exposed to aqueous ammonium hydroxide.


STABILIZED CARBANIONS (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ H ₆	 (79)	632
"	 (85)	632
—	 I	
—	I X ¹ = COC ₆ H ₅ , X ² = H, X ³ = NO ₂ (62)	83,87
—	I X ¹ = X ² = H, X ³ = COC ₆ H ₄ Cl-4 (67)	87,83
—	I X ¹ = X ² = H, X ³ = COC ₆ H ₄ Br-4 (90)	87,83
—	I X ¹ = X ² = H, X ³ = COC ₆ H ₄ OCH ₃ -4 (90)	87,83
—	I X ¹ = X ² = H, X ³ = COC ₆ H ₄ CH ₃ -4 (98)	87,83
—	I X ¹ = X ² = H, X ³ = COC ₆ H ₅ (92)	87,83
C ₆ H ₆	 (70)	632

^d The initial product was quenched with CF₃CO₂H at low temperature and exposed to ceric ammonium nitrate.

^e The initial product was oxidized with oxygen under basic conditions.

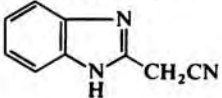
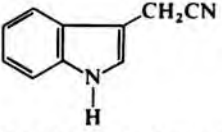
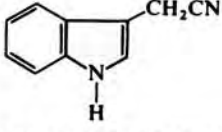
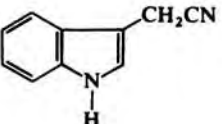
TABLE III. ACYLATION OF NITRILE-STABILIZED CARBANIONS WITH CARBOXYLIC

No. of C Atoms	Nucleophile	Electrophile	Base
C ₃ (Contd.)	C ₂ H ₅ CN	C ₆ H ₅ CH=CHCO ₂ C ₄ H ₉ - <i>t</i>	LiNH ₂
C ₄	<i>n</i> -C ₃ H ₇ CN	CH ₃ CO ₂ C ₂ H ₅ <i>n</i> -C ₃ H ₇ CO ₂ C ₂ H ₅ C ₆ H ₅ CO ₂ C ₂ H ₅ C ₆ H ₅ CH=CHCO ₂ R	NaNH ₂ LiN(C ₂ H ₅) ₂ " LiNH ₂ "
C ₅	<i>n</i> -C ₄ H ₉ CN <i>i</i> -C ₄ H ₉ CN <i>n</i> -C ₄ H ₉ CN	CH ₃ CO ₂ C ₂ H ₅ (C ₂ H ₅ O) ₂ C=O C ₆ H ₅ CO ₂ CH ₃ 3-ClC ₆ H ₄ CO ₂ CH ₃ C ₆ H ₅ CO ₂ C ₂ H ₅	NaNH ₂ LDA NaNH ₂ " "
C ₆	<i>n</i> -C ₅ H ₁₁ CN	(C ₂ H ₅ O) ₂ CO (CO ₂ C ₂ H ₅) ₂ C ₆ H ₅ CO ₂ C ₂ H ₅	LDA NaOC ₂ H ₅ NaNH ₂
C ₇	2-Pyridylacetonitrile	XCH ₂ COCl	—
		CH ₃ CHXCOCl	—
		C ₂ H ₅ CHXCOCl	—
	4-Pyridylacetonitrile	(CH ₃ CO) ₂ O	—
	2-Pyridylacetonitrile	"	—
		(C ₂ H ₅ O) ₂ CO	LDA
	2-Pyridylacetonitrile	(C ₂ H ₅ CO) ₂ O C ₆ H ₅ CHXCOCl	— —
C ₈	<i>n</i> -C ₇ H ₁₅ CN	C ₆ H ₅ NHCH ₂ CH ₂ CO ₂ C ₂ H ₅ ClCO ₂ C ₂ H ₅ "	<i>t</i> -C ₄ H ₉ ONa LDA NaN[Si(CH ₃) ₃] ₂
	C ₆ H ₅ CH ₂ CN	HCO ₂ C ₂ H ₅ CH ₃ CO ₂ C ₂ H ₅ "	NaOC ₂ H ₅ " NaNH ₂ "
	<i>n</i> -C ₇ H ₁₅ CN	C ₂ H ₅ CO ₂ CH ₃ (C ₂ H ₅ O) ₂ CO "	LDA NaN[Si(CH ₃) ₃] ₂ "
	C ₆ H ₁₁ CH ₂ CN	"	LDA
	C ₆ H ₅ CH ₂ CN	"	NaOH <i>n</i> -C ₄ H ₉ Li NaNH ₂ "
	4-ClC ₆ H ₄ CH ₂ CN	"	NaOC ₂ H ₅
	C ₆ H ₅ CH ₂ CN	(CO ₂ C ₂ H ₅) ₂	"
	4-XC ₆ H ₄ CH ₂ CN	"	"

ESTERS, ANHYDRIDES, ACID CHLORIDES, NITRILES, AND DIALKYL CARBONATES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NH ₃	C ₆ H ₅ CH=CHCOCH(CH ₃)CN (75)	295
"	CH ₃ COCH(C ₂ H ₅)CN (66)	294
THF, -75°	<i>n</i> -C ₃ H ₇ COCH(C ₂ H ₅)CN (74)	302
"	C ₆ H ₅ COCH(C ₂ H ₅)CN (55)	302
"	C ₆ H ₅ CH=CHCOCH(C ₂ H ₅)CN I	
NH ₃	I, R = C ₂ H ₅ (53)	295
"	I, R = C ₄ H ₉ - <i>t</i> (40)	295
"	CH ₃ COCH(C ₃ H ₇ - <i>n</i>)CN (74)	294
THF	<i>i</i> -C ₃ H ₇ CH(CO ₂ C ₂ H ₅)CN (56)	292
NH ₃ , Et ₂ O	<i>n</i> -C ₃ H ₇ CH(COC ₆ H ₅)CN (78)	54
"	<i>n</i> -C ₃ H ₇ CH(COC ₆ H ₄ Cl-3)CN (70)	54
NH ₃	<i>n</i> -C ₃ H ₇ CH(COC ₆ H ₅)CN (71)	294
THF	<i>n</i> -C ₄ H ₉ CH(CO ₂ C ₂ H ₅)CN (76)	292
C ₂ H ₅ OH	<i>n</i> -C ₄ H ₉ CH(COCO ₂ C ₂ H ₅)CN (-)	306
NH ₃	C ₆ H ₅ COCH(C ₄ H ₉ - <i>n</i>)CN (66)	294
—	2-C ₃ H ₄ NCH(COCH ₂ X)CN I	303
—	I, X = Cl or Br (-)	
—	2-C ₃ H ₄ NCH[COCH(CH ₃)X]CN I	303
—	I, X = Cl or Br (-)	
—	2-C ₃ H ₄ NCH[(COCH(C ₂ H ₅)X]CN I	
—	I, X = Cl or Br (-)	303
(CH ₃ CO) ₂ O	(4-C ₃ H ₄ N)C(CN)=C(OH)CH ₃ (-)*	259
CH ₃ CO ₂ H	(2-C ₃ H ₄ N)C(CN)=C(OH)CH ₃ (98, crude)	259
—	C ₅ H ₉ CH(CO ₂ C ₂ H ₅)CN (79)	292
C ₂ H ₅ CO ₂ H	2-C ₃ H ₄ NC(CN)=C(OH)C ₂ H ₅ (-)	259
—	(2-C ₃ H ₄ N)CH[COCH(C ₆ H ₅)X]CN I	303
—	I X = Cl or Br (-)	
Py	2-C ₃ H ₄ NC(CN)=C(OH)CH ₂ CH ₂ NHC ₆ H ₅ (50)	300
THF	<i>n</i> -C ₆ H ₁₃ CH(CO ₂ C ₂ H ₅)CN (85-87)	292
"	" (49)	292
C ₂ H ₅ OH	C ₆ H ₅ CH(CHO)CN (-)	297
"	C ₆ H ₅ CH(COCH ₃)CN (-)	297
NH ₃ , Et ₂ O	" (70)	54,293
"	C ₆ H ₅ CH(COC ₂ H ₅)CN (74)	54
THF	<i>n</i> -C ₆ H ₁₃ CH(CO ₂ C ₂ H ₅)CN (76)	292
"	" (11)	292
"	C ₆ H ₁₁ CH(CO ₂ C ₂ H ₅)CN (86)	292
NH ₃	C ₆ H ₅ CH(CO ₂ C ₂ H ₅)CN (50-60)	289
THF	" (79)	47
C ₆ H ₆	" (-)	290
C ₂ H ₅ OH	4-ClC ₆ H ₄ CH(CO ₂ C ₂ H ₅)CN (77)	291
"	C ₆ H ₅ CH(COCO ₂ C ₂ H ₅)CN (-)	305,297
"	4-XC ₆ H ₄ CH(COCO ₂ C ₂ H ₅)CN I	
"	I X = Cl (-)	305
"	I X = F (-)	305

TABLE III. ACYLATION OF NITRILE-STABILIZED CARBANIONS WITH CARBOXYLIC

No. of C Atoms	Nucleophile	Electrophile	Base
C ₈ (Contd.)	C ₆ H ₅ CH ₂ CN	C ₆ H ₅ COCl C ₆ H ₅ CH ₂ CN C ₆ H ₅ CO ₂ CH ₃ "	C ₁₀ H ₈ Na <i>t</i> -C ₄ H ₉ OK NaNH ₂ <i>n</i> -C ₄ H ₉ Li NaOC ₂ H ₅ NaOC ₂ H ₅ <i>t</i> -C ₄ H ₉ OK NaOC ₂ H ₅ "
	4-ClC ₆ H ₄ CH ₂ CN	C ₆ H ₅ CO ₂ C ₂ H ₅ C ₆ H ₅ CH ₂ CO ₂ C ₂ H ₅ C ₆ H ₅ CO ₂ C ₂ H ₅ C ₆ H ₅ CH(CN)COCO ₂ C ₂ H ₅ 4-XC ₆ H ₄ CH ₂ CN	C ₆ H ₅ CO ₂ C ₂ H ₅ NaOC ₂ H ₅ NaOC ₂ H ₅ NaOC ₂ H ₅ NaOC ₂ H ₅ "
	C ₆ H ₅ CH ₂ CN	C ₆ H ₅ CH(CN)COCO ₂ C ₂ H ₅	NaOC ₂ H ₅
	4-CH ₃ OC ₆ H ₄ CH ₂ CN	4-CH ₃ OC ₆ H ₄ CH(CN)COCO ₂ C ₂ H ₅ CH ₃ CO ₂ C ₂ H ₅ "	NaOC ₂ H ₅ <i>t</i> -C ₄ H ₉ OK LDA NaOC ₂ H ₅ "
C ₉	4-CH ₃ C ₆ H ₄ CH ₂ CN	(CO ₂ C ₂ H ₅) ₂ "	NaOC ₂ H ₅ "
		C ₆ H ₅ NHCH ₂ CH ₂ CO ₂ CH ₃	<i>t</i> -C ₄ H ₉ ONa
C ₁₀	4-CH ₃ C ₆ H ₄ CH ₂ CN	4-CH ₃ C ₆ H ₄ CH(CN)COCO ₂ C ₂ H ₅	NaOC ₂ H ₅
	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN	HCO ₂ C ₂ H ₅ ClCO ₂ C ₂ H ₅ "	KOCH ₃ NaNH ₂ K ₂ CO ₃ , dibenzo-18-crown-6
		(CH ₃ O) ₂ CO	NaOCH ₃
	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN	CH ₃ CO ₂ C ₂ H ₅ "	NaOC ₂ H ₅ LDA
		(C ₂ H ₅ O) ₂ CO	NaH
3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN	(CO ₂ C ₂ H ₅) ₂	NaOC ₂ H ₅	
	(CO ₂ C ₂ H ₅) ₂	NaH	

ESTERS, ANHYDRIDES, ACID CHLORIDES, NITRILES, AND DIALKYL CARBONATES (Continued)

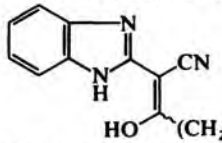
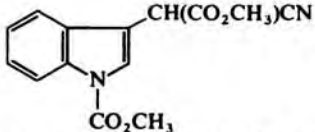
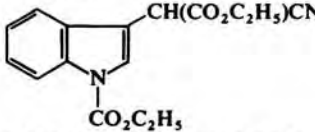
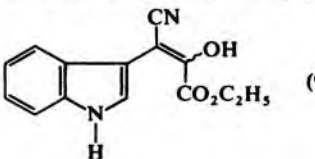
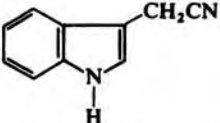
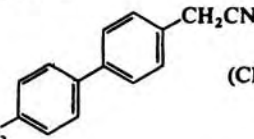
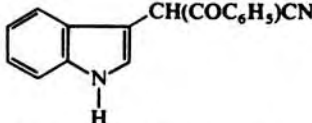
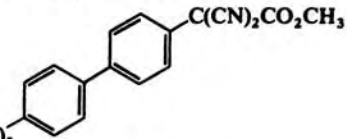
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF	C ₆ H ₅ C(COC ₆ H ₅) ₂ CN (34)	198
<i>t</i> -C ₄ H ₉ OH	C ₆ H ₅ CH ₂ C(NH ₂)=C(C ₆ H ₅)CN (-)	258
NH ₃ , Et ₂ O	C ₆ H ₅ COCH(C ₆ H ₅)CN (70)	54
THF, 25°	" (35-71)	47
C ₂ H ₅ OH	" (-)	297
C ₂ H ₅ OH	4-ClC ₆ H ₄ CH(COCH ₂ C ₆ H ₅)CN (74-82)	541
DMF	4-ClC ₆ H ₄ CH(COC ₆ H ₅)CN (30)	296
C ₂ H ₅ OH	[C ₆ H ₅ CH(CN)CO] ₂ (-)	305
"	[4-XC ₆ H ₄ CH(CN)CO] ₂ I	
"	I X = Cl (-)	305
"	I X = F (-)	305
C ₂ H ₅ OH	4-CH ₃ OC ₆ H ₄ CH(CN)COCOCH(CN)C ₆ H ₅ (-)	305
DMF	4-CH ₃ OC ₆ H ₄ CH(COCH ₃)CN (60)	296
THF	" (97)	301
C ₂ H ₅ OH	4-CH ₃ OC ₆ H ₄ CH(COCO ₂ C ₂ H ₅)CN (-)	305
"	4-CH ₃ C ₆ H ₄ CH(COCO ₂ C ₂ H ₅)CN (-)	305
	 (62)	300
C ₂ H ₅ OH	[4-CH ₃ C ₆ H ₄ CH(CN)CO] ₂ (-)	305
Et ₂ O	3,4-(CH ₃ O) ₂ C ₆ H ₃ C(CN)=CHOH (-)	258
"	C ₆ H ₅ C(C ₂ H ₅)(CO ₂ C ₂ H ₅)CN (-)	289
-	" (43)	304
CH ₃ OH	 (60)	299
C ₂ H ₅ OH	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH(COCH ₃)CN (-)	258
THF	" (90)	301
Et ₂ O	 (50)	299
C ₂ H ₅ OH	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH(COCO ₂ C ₂ H ₅)CN (86)	306
-	 (95)	299

TABLE III. ACYLATION OF NITRILE-STABILIZED CARBANIONS WITH CARBOXYLIC

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₀ (Contd.)	C ₆ H ₅ CH(C ₂ H ₅)CN	C ₆ H ₅ COCl	K ₂ CO ₃ , dibenzo-18-crown-6
		C ₆ H ₅ CO ₂ C ₂ H ₅	NaH
C ₁₄	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN (C ₆ H ₅) ₂ CHCN	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN C ₂ H ₅ OCOCOCI	<i>t</i> -C ₄ H ₉ OK NaNH ₂ or NaH
C ₁₆		(CH ₃ O) ₂ CO	NaOCH ₃
C ₁₈	<i>n</i> -C ₁₇ H ₃₅ CN	(C ₂ H ₅ O) ₂ CO	LDA





^a This product was obtained after recrystallization of the initial *C,N*-diacetyl adduct.

ESTERS, ANHYDRIDES, ACID CHLORIDES, NITRILES, AND DIALKYL CARBONATES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	C ₆ H ₅ C(C ₂ H ₅)(COC ₆ H ₅)CN (35)	304
—	 (86)	299
<i>t</i> -C ₄ H ₉ OH	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ C(NH ₂)=C[C ₆ H ₃ (OCH ₃) ₂ -3,4]CN (—)	258
—	(C ₆ H ₅) ₂ C(COCO ₂ C ₂ H ₅)CN (—)	835
Toluene	 (—) ^b	836
THF	CH ₃ O ₂ CC(CN) ₂ <i>n</i> -C ₁₆ H ₃₃ CH(CO ₂ C ₂ H ₅)CN (81)	292

^b The initial product was treated with ClCN.

TABLE IV. ADDITION OF NITRILE-STABILIZED CARBANIONS TO

No. of C Atoms	Nucleophile	Electrophile	Base or Metal
C ₂	CH ₃ CN	HCHO	Alkali metal hydroxide, silica gel
		CH ₃ CHO	C ₁₀ H ₈ Na <i>i</i> -C ₄ H ₉ Li
	BrCH ₂ CN CH ₃ CN	(CH ₃) ₂ CO	<i>i</i> -C ₄ H ₉ Li (2 eq) NaN[Si(CH ₃) ₃] ₂
		<i>n</i> -C ₃ H ₇ CHO (C ₂ H ₅) ₂ CO	Zn KOH
		<i>i</i> -C ₃ H ₇ COCH ₃	<i>n</i> -C ₄ H ₉ Li LiN(C ₂ H ₅) ₂
	BrCH ₂ CN CH ₃ CN		<i>n</i> -C ₄ H ₉ Li
		(C ₂ H ₅) ₂ CO <i>i</i> -C ₃ H ₇ COCH ₃ <i>n</i> -C ₄ H ₉ COCH ₃	Zn LiN(C ₂ H ₅) ₂
	BrCH ₂ CN CH ₃ CN		KOH
		"	Zn, HgCl ₂
	C ₂	BrCH ₂ CN CH ₃ CN	<i>n</i> -C ₆ H ₁₃ CHO (<i>n</i> -C ₃ H ₇) ₂ CO
			"
BrCH ₂ CN CH ₃ CN			"
		C ₆ H ₅ CHO	NaN[Si(CH ₃) ₃] ₂ LiN(C ₂ H ₅) ₂ <i>n</i> -C ₄ H ₉ Li
ClCH ₂ CN BrCH ₂ CN		"	"
		4-ClC ₆ H ₄ CHO	Cl ₂ BN(C ₂ H ₅) ₂ , N(C ₂ H ₅) ₃
		4-O ₂ NC ₆ H ₄ CHO	"
		C ₆ H ₅ CHO	Zn
		"	"
		2-ClC ₆ H ₄ CHO	"
	3-ClC ₆ H ₄ CHO	Zn, HgCl ₂	
	4-ClC ₆ H ₄ CHO	Zn	

ALDEHYDES, KETONES, IMINES, ALKENES, AND ALKYNES








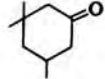

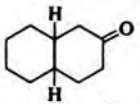
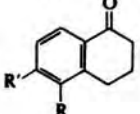
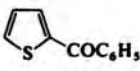
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Gas phase, 300-600°	CH ₂ =CHCN (-)	837
THF Et ₂ O, -78°	HO(CH ₂) ₂ CN (1-8), 2,4,6-trimethyltriazine (-) (CH ₃) ₃ SiOCH(CH ₃)CH ₂ CN (10) ^a , [(CH ₃) ₃ SiOCH(CH ₃) ₂ CHCN (70) ^a , [(CH ₃) ₃ SiOCH(CH ₃) ₃ CCN (5) ^a	838 19
Et ₂ O, -78° Et ₂ O, 20° THF or DMSO CH ₃ CN THF, hexane, -80° HMPA, C ₆ H ₆ , -70°	[(CH ₃) ₂ C(OSi(CH ₃) ₃) ₂ CHCN (47) (CH ₃) ₂ C[OSi(CH ₃) ₃]C ₂ H ₅ CN (39, 90% pure) <i>n</i> -C ₃ H ₇ CH(OH)CH ₂ CN (30) (C ₂ H ₅) ₂ C=CHCN (35) (C ₂ H ₅) ₂ COHCH ₂ CN (68) <i>i</i> -C ₃ H ₇ COH(CH ₂) ₂ CN (95)	19 21 355 349 106 326
THF, hexane, -80°	HO CH ₂ CN  (61)	106
THF or DMSO HMPA, C ₆ H ₆ , -70°	(C ₂ H ₅) ₂ COHCH ₂ CN (54) <i>i</i> -C ₃ H ₇ COH(CH ₂) ₂ CN (42) <i>n</i> -C ₄ H ₉ COH(CH ₂) ₂ CN (88)	355 355 326
CH ₃ CN	 I.  II (70, I/II = 4.5)	349
THF HMPA, C ₆ H ₆ , -70° CH ₃ CN	HO CH ₂ CN  (70) <i>n</i> -C ₆ H ₁₃ CHOHCH ₂ CN (70) (<i>n</i> -C ₃ H ₇) ₂ C=CHCN	352 326 349
"	 I.  II (78, I/II = 0.98)	349
"	 (78)	349
Ether, 20° HMPA, C ₆ H ₆ , -70° THF, -78° THF, hexane, -80°	C ₆ H ₅ CH(OSi(CH ₃) ₃)CH ₂ CN (57) C ₆ H ₅ CHOHCH ₂ CN (80) " (83) " (78) C ₆ H ₅ CH(CH ₂ CN)N(C ₂ H ₅) ₂ (51) 4-ClC ₆ H ₄ CH(CH ₂ CN)N(C ₂ H ₅) ₂ (33) 4-O ₂ NC ₆ H ₄ CH(CH ₂ CN)N(C ₂ H ₅) ₂ (7) C ₆ H ₅ CHOHCH ₂ CN (24) " (48)	21 326 325 106 358 358 353 353,351
Et ₂ O, C ₆ H ₆	2-ClC ₆ H ₄ CHOHCH ₂ CN (43)	839
"	3-ClC ₆ H ₄ CHOHCH ₂ CN (28)	839
"	" (51)	839
"	4-ClC ₆ H ₄ CHOHCH ₂ CN (53)	839

TABLE IV. ADDITION OF NITRILE-STABILIZED CARBANIONS TO

No. of C Atoms	Nucleophile	Electrophile	Base or Metal	
C ₂ (Contd.)	CH ₃ CN	C ₆ H ₅ COCH ₃	KOH	
		"	NaNH ₂	
		"	<i>n</i> -C ₄ H ₉ Li	
	ClCH ₂ CN BrCH ₂ CN	4-CH ₃ OC ₆ H ₄ CHO	Cl ₂ BN(C ₂ H ₅) ₂ , N(C ₂ H ₅) ₃	
		C ₆ H ₅ COCH ₃	Zn	
		2-CH ₃ OC ₆ H ₄ CHO	Zn, HgCl ₂	
		3-CH ₃ OC ₆ H ₄ CHO	"	
		4-CH ₃ OC ₆ H ₄ CHO	"	
		3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO	"	
	CH ₃ CN	C ₆ H ₅ COCH ₃	"	
		"	Zn	
		(<i>n</i> -C ₄ H ₉) ₂ CO	KOH	
		3,6-Dimethyl-5-hepten-2-one	NaOH	
			Base ^d	
	BrCH ₂ CN CH ₃ CN	(n-C ₄ H ₉) ₂ CO	C ₆ H ₅ COC ₃ H _{7-n}	Zn, HgCl ₂
KOH				
		C ₄ H _{9-t}	Base ^d	Base ^d
				Base ^d
				Base ^d
				RZnBr ^d
				RZnBr ^d
				RLi ^d
		"	"	"
				"
		R	R'	<i>n</i> -C ₄ H ₉ Li
				<i>n</i> -C ₄ H ₉ Li
	COC ₆ H ₅	"	<i>n</i> -C ₄ H ₉ Li	
Cyclododecanone	"	"	KOH	

ALDEHYDES, KETONES, IMINES, ALKENES, AND ALKYNES (Continued)

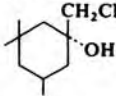
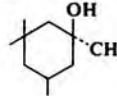
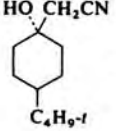
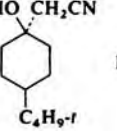
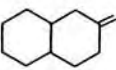
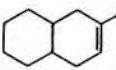
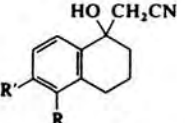
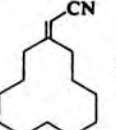
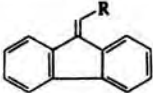
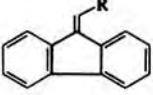


Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
CH ₃ CN	C ₆ H ₅ C(CH ₃)=CHCN (15, <i>E/Z</i> = 4.1)	349
Et ₂ O	C ₆ H ₅ C(OH)(CH ₃)CH ₂ CN (-)	322
THF, hexane, -80°	" (70)	106
-	4-CH ₃ OC ₆ H ₄ CH(CH ₂ CN)N(C ₂ H ₅) ₂ (61)	358
-	C ₆ H ₅ C(CH ₃)=CHCN (44)	353
THF	2-CH ₃ OC ₆ H ₄ CHOHCH ₂ CN (70)	354
"	3-CH ₃ OC ₆ H ₄ CHOHCH ₂ CN (74)	354
"	4-CH ₃ OC ₆ H ₄ CHOHCH ₂ CN (62)	354
"	3,4-(CH ₃ O) ₂ C ₆ H ₃ CHOHCH ₂ CN (76)	354
"	C ₆ H ₅ C(CH ₃)=CHCN (-), C ₆ H ₅ COH(CH ₃)CH ₂ CN (-)	352
-	C ₆ H ₅ C(OH)(CH ₃)CH ₂ CN (68)	353,355
CH ₃ CN	(<i>n</i> -C ₄ H ₉) ₂ C=CHCN (65)	349
"	3,4,7-Trimethyl-2,6-octadienenitrile (-)	348
THF	 I,  II	840
THF	I:II = 98:2 (-)	
CH ₃ CN	(<i>n</i> -C ₄ H ₉) ₂ COHCH ₂ CN (27)	352
	C ₆ H ₅ (C ₃ H _{7-n})C=CHCN (30; <i>E/Z</i> = 3.6)	349
	 I,  II,	
	C ₄ H _{9-t}	
THF	I:II = 75:25 (-)	840
THF	I:II = 85:15 (-)	840
18-Crown-6, THF	I:II = 80:20 (-)	840
THF	I:II = 67:33 (53)	841
THF, HMPT	I:II = 72:28 (52)	841
Pentane, Et ₂ O	I:II = 65:35 (67)	841
C ₆ H ₆ , HMPT	I:II = 65:35 (53)	841
"	 I,  II (80, I/II = 3.4)	349
THF		328
	I R = R' = H (-)	
	I R = H, R' = OCH ₃ (-)	
	I R = OCH ₃ , R' = H (-)	
THF, 0°	[(2-C ₄ H ₉ S)(OH)C ₆ H ₅] ₂ CHCN	336
CH ₃ CN	 (45)	349

TABLE IV. ADDITION OF NITRILE-STABILIZED CARBANIONS TO

No. of C Atoms	Nucleophile	Electrophile	Base or Metal
C ₂ (Contd.)	CH ₃ CN		LiNH ₂
C ₃	C ₂ H ₅ CN	HCHO	Alkali metal hydroxide, silica gel
	CH ₃ CHBrCN	C ₆ H ₅ CHO	Zn
	C ₂ H ₅ CN	n-C ₆ H ₁₃ COCH ₃	KOH
		6-Methyl-5-hepten-2-one	"
	CH ₃ CHBrCN	C ₆ H ₅ COCH ₃	Zn
	C ₂ H ₅ CN	C ₆ H ₅ ¹⁴ COC ₂ H ₅	NaNH ₂
		C ₆ H ₅ COC ₂ H ₅	"
			LiNH ₂
C ₄	i-C ₃ H ₇ CN	HCHO	Li(C ₂ H ₅)
		CH ₃ CHO	"
		n-C ₃ H ₇ CHO	"
		CH ₃ CH=CHCHO	"
	C ₂ H ₅ CHBrCN	n-C ₃ H ₇ CHO	Zn
		C ₂ H ₅ COCH ₃	"
	n-C ₃ H ₇ CN	i-C ₃ H ₇ COCH ₃	Li(C ₂ H ₅) ₂
	i-C ₃ H ₇ CN	C ₂ H ₅ COC ₂ H ₅	"
	n-C ₃ H ₇ CN	n-C ₄ H ₉ COCH ₃	"
	i-C ₃ H ₇ CN	i-C ₄ H ₉ COCH ₃	"
			"
		C ₆ H ₅ CHO	"
	(CH ₃) ₂ CBrCN	"	Zn
	n-C ₃ H ₇ CN	(CH ₃) ₂ C=CH(CH ₂) ₂ COCH ₃	KOH or n-C ₈ H ₁₇ ONa
	(CH ₃) ₂ CBrCN	C ₆ H ₅ COCH ₃	Zn
	CH ₃ O(CH ₂) ₂ CN		NaOCH ₃
		3-Methoxy-4,5-methylenedioxybenzaldehyde	"
		3,5-Dimethoxy-4-methylbenzaldehyde	"

ALDEHYDES, KETONES, IMINES, ALKENES, AND ALKYNES (Continued)

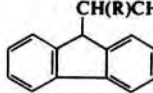
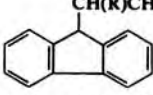

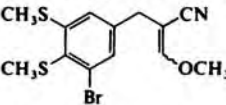
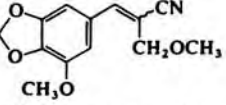
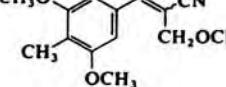
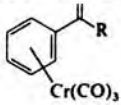
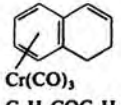
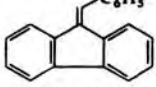

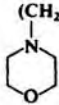
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NH ₃ , Et ₂ O	 I	396
	I R = C ₆ H ₅ (50)	
	I R = C ₄ H ₉ O-2 (87)	
Gas phase, 300-600°	CH ₂ =C(CH ₃)CN (-)	837
	C ₆ H ₅ CHOHCH(CH ₃)CN (82)	353
	n-C ₆ H ₁₃ C(CH ₃)=C(CH ₃)CN (48)	350
	(CH ₃) ₂ C=CH(CH ₂) ₂ C(CH ₃)=C(CH ₃)CN (-)	350
	C ₆ H ₅ COH(CH ₃)CH(CH ₃)CN (77)	353
	(C ₆ H ₅) ₂ ¹⁴ COHCH(CH ₃)CH ₂ NH ₂ (39) ^b	335
Et ₂ O	(C ₆ H ₅) ₂ COHCH(CH ₃)CN (-)	323,842
	 I	396
	I R = C ₆ H ₅ (61)	
	I R = C ₄ H ₉ O-2 (70)	
HMPA, C ₆ H ₆ , -70°	HOCH ₂ C(CH ₃) ₂ CN (70)	326
"	CH ₃ CHOHC(CH ₃) ₂ CN (85)	326
"	n-C ₃ H ₇ CHOHC(CH ₃) ₂ CN (85)	326
"	CH ₃ CH=CHCHOHC(CH ₃) ₂ CN (57)	326
THF or DMSO	n-C ₃ H ₇ CHOHCH(CH ₃)CN (66)	355
"	C ₂ H ₅ C(CH ₃)OHCH(CH ₃)CN (57)	355
HMPA, C ₆ H ₆ , -70°	i-C ₃ H ₇ COH(CH ₃)CH(CH ₃)CN (63)	326
"	(C ₂ H ₅) ₂ COHC(CH ₃) ₂ CN (88)	326
"	n-C ₄ H ₉ COH(CH ₃)CH(CH ₃)CN (90)	326
"	i-C ₄ H ₉ COH(CH ₃)C(CH ₃) ₂ CN (90)	326
"	HO C(CH ₃) ₂ CN	
"	 (85)	326
"	C ₆ H ₅ CHOHC(CH ₃) ₂ CN (77)	326
"	C ₆ H ₅ CHOHC(CH ₃) ₂ CN (84)	353
C ₆ H ₆	(CH ₃) ₂ C=CH(CH ₂) ₂ C(CH ₃)=C(CH ₃)CN (16)	350
"	C ₆ H ₅ COH(CH ₃)C(CH ₃) ₂ CN (46)	353
CH ₃ OH	 (-)	843
"	 (83)	346
"	 (67)	346

TABLE IV. ADDITION OF NITRILE-STABILIZED CARBANIONS TO

No. of C Atoms	Nucleophile	Electrophile	Base or Metal
C ₄ (Contd.)	<i>i</i> -C ₃ H ₇ CN		LDA
			"
	<i>n</i> -C ₃ H ₇ CN	C ₆ H ₅ COC ₆ H ₅	LiN(C ₂ H ₅) ₂
C ₃	HO ₂ C(CH ₂) ₃ CN		LiNH ₂
		4-XC ₆ H ₄ COC ₆ H ₅	"
		(C ₆ H ₅) ₂ C=NCOC ₆ H ₅	"
C ₆	3-Thienylacetonitrile	C ₂ H ₅ COCH ₃	NaOC ₂ H ₅
	2-Thienylacetonitrile		NaOC ₂ H ₅
	HO ₂ C(CH ₂) ₄ CN	(C ₆ H ₅) ₂ C=NCOC ₆ H ₅	LiNH ₂
C ₇	C ₆ H ₁₁ CN	HCHO	LiN(C ₂ H ₅) ₂
	2-Pyridylacetonitrile	CH ₃ CHO	Piperidine
	C ₆ H ₁₁ CN	CH ₃ COCH ₃	LiN(C ₂ H ₅) ₂
	4-Pyridylacetonitrile	<i>i</i> -C ₃ H ₇ CHO	"
		<i>i</i> -C ₄ H ₉ COCH ₃	"
		4-H ₂ NC ₆ H ₄ CHO	NaOCH ₃
		4-O ₂ NC ₆ H ₄ CHO	"
		4-(CH ₃) ₂ NC ₆ H ₄ CHO	"
	3-Pyridylacetonitrile	"	"
	4-Pyridylacetonitrile	"	"
	(CH ₂) ₂ CN	"	"
		3,5-Dimethoxy-4-thiomethoxybenzaldehyde	"

ALDEHYDES, KETONES, IMINES, ALKENES, AND ALKYNES (Continued)

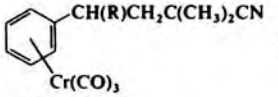
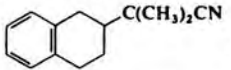
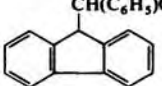
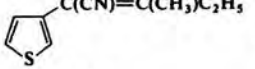
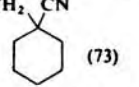

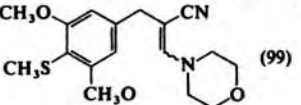
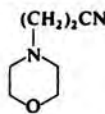


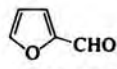

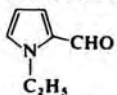
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF, -78°	 I I R = H (92) I R = CH ₃ (34) I R = SC ₂ H ₅ (62)	844
"	 (95-100) ^c	844
HMPA, C ₆ H ₆	(C ₆ H ₅) ₂ COHC(CH ₃) ₂ CN (92)	326
NH ₃ , Et ₂ O	 (54)	396
NH ₃	4-XC ₆ H ₄ COH(C ₆ H ₅)CH[(CH ₂) ₂ CO ₂ H]CN I I X = H (-) I X = Cl (-)	112
"	(C ₆ H ₅) ₂ C(NHCOC ₆ H ₅)CH[(CH ₂) ₂ CO ₂ H]CN (-)	112
C ₂ H ₅ OH	 (50)	356
C ₂ H ₅ OH	C(C ₆ H ₅ S-2)CN (-)	339
NH ₃	(C ₆ H ₅) ₂ C(NHCOC ₆ H ₅)CH[(CH ₂) ₂ CO ₂ H]CN (-)	112
HMPA, C ₆ H ₆ , -70°	 (73)	326
C ₆ H ₆ , CH ₃ CO ₂ H	(2-C ₃ H ₄ N)C(CN)=CHCH ₃ (74)	259
HMPA, C ₆ H ₆	 I	326
"	I R = C(CH ₃) ₂ OH (92)	326
"	I R = CHOHC ₂ H ₅ - <i>i</i> (90)	326
"	I R = COH(CH ₃)C ₄ H ₉ - <i>i</i> (78)	342
CH ₃ OH	4-C ₃ H ₄ NC(CN)=CHC ₆ H ₄ NH ₂ -4 (-)	342
"	4-C ₃ H ₄ NC(CN)=CHC ₆ H ₄ NO ₂ -4 (-)	342
"	3-C ₃ H ₄ NC(CN)=CHC ₆ H ₄ N(CH ₃) ₂ -4 (-)	342
"	4-C ₃ H ₄ NC(CN)=CHC ₆ H ₄ N(CH ₃) ₂ -4 (-)	342
DMSO	 (99)	843

TABLE IV. ADDITION OF NITRILE-STABILIZED CARBANIONS TO

No. of C Atoms	Nucleophile	Electrophile	Base or Metal
C ₇ (Contd.)		3,5-Dimethoxy-4-methylbenzaldehyde	NaOCH ₃
C ₈	C ₆ H ₅ CH ₂ CN	HCHO (HCHO) _n CH ₃ CHO C ₂ H ₅ CHO <i>n</i> -C ₃ H ₇ CHO <i>i</i> -C ₃ H ₇ CHO <i>n</i> -C ₄ H ₉ CHO <i>i</i> -C ₄ H ₉ CHO	KOH, Fe(CO) ₅ NaOCH ₃ " " " " " "
			NaOC ₂ H ₅
			"
			NaOH
		<i>n</i> -C ₅ H ₁₁ CHO	NaOCH ₃
			NaOC ₂ H ₅
		C ₆ H ₅ CHO	Cl ₂ , BN(C ₂ H ₅) ₂ , CH ₂ Cl ₂
		"	NaOH
		"	NaOC ₂ H ₅
		"	NaOH, polyethylene glycol
		"	KOH, Fe(CO) ₅
		4-ClC ₆ H ₄ CHO	NaOH
		2-ClC ₆ H ₄ CHO	"
			"
	3-O ₂ NC ₆ H ₄ CH ₂ CN	C ₆ H ₅ CHO	"
	4-O ₂ NC ₆ H ₄ CH ₂ CN	"	NaOC ₂ H ₅
	4-FC ₆ H ₄ CH ₂ CN	"	[C ₆ H ₅ CH ₂ N(CH ₃) ₃]OH
	4-ClC ₆ H ₄ CH ₂ CN	"	NaOCH ₃
	C ₆ H ₅ CH ₂ CN	"	"
		4-CH ₃ OC ₆ H ₄ CHO	NaOH
		4-CH ₃ C ₆ H ₄ CHO	"
		3,4-(CH ₂ O ₂)C ₆ H ₃ CHO	"
		C ₆ H ₅ COC ₂ H ₅	NaNH ₂
		4-(CH ₃) ₂ NC ₆ H ₄ CHO	NaOC ₂ H ₅
		"	"
	3-O ₂ NC ₆ H ₄ CH ₂ CN	4-CH ₃ OC ₆ H ₄ COC ₂ H ₅	NaNH ₂
	4-O ₂ NC ₆ H ₄ CH ₂ CN	1-C ₁₀ H ₇ CHO	NaOH

ALDEHYDES, KETONES, IMINES, ALKENES, AND ALKYNES (Continued)

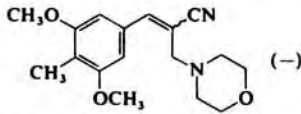
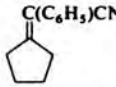
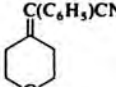
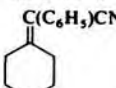
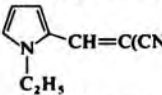


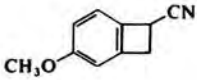
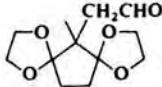
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
DMSO	 (-)	346
C ₂ H ₅ OH	C ₆ H ₅ CH(CH ₃)CN (67)	316
Toluene	[C ₆ H ₅ C(CN)(CH ₂ OH)] ₂ CH ₂ (65-70)	357
C ₂ H ₅ OH, -5°	C ₆ H ₅ C(CN)=CHCH ₃ (-)	341
CH ₃ OH	C ₆ H ₅ C(CN)=CHC ₂ H ₅ (-)	343
"	C ₆ H ₅ C(CN)=CH(C ₃ H ₇ - <i>n</i>) (-)	343
"	C ₆ H ₅ C(CN)=CH(C ₃ H ₇ - <i>i</i>) (-)	343
"	C ₆ H ₅ C(CN)=CH(C ₄ H ₉ - <i>n</i>) (-)	343
"	C ₆ H ₅ C(CN)=CH(C ₄ H ₉ - <i>i</i>) (-)	343
C ₂ H ₅ OH	 (-)	339
"	 (20)	753
"	C ₆ H ₅ C(CN)=CH(C ₆ H ₅ O-2)	753
CH ₃ OH	C ₆ H ₅ C(CN)=CH(C ₃ H ₁₁ - <i>n</i>) (-)	343
C ₂ H ₅ OH	 (90)	339
(C ₂ H ₅) ₃ N	C ₆ H ₅ CH[N(C ₂ H ₅) ₂]CH(C ₆ H ₅)CN (28)	358
C ₂ H ₅ OH	C ₆ H ₅ CH=C(C ₆ H ₅)CN (88-100)	308
"	" (83-91)	340,337
"	" (71)	845
Toluene	C ₆ H ₅ CH ₂ CH(C ₆ H ₅)CN (-)	316
C ₂ H ₅ OH	4-ClC ₆ H ₄ CH=C(C ₆ H ₅)CN (88-100)	308
"	2-ClC ₆ H ₄ CH=C(C ₆ H ₅)CN (88-100)	308
"	 (91)	250,251
"	3-O ₂ NC ₆ H ₄ C(CN)=CHC ₆ H ₅ (30)	337
"	4-O ₂ NC ₆ H ₄ C(CN)=CHC ₆ H ₅ (90)	337
CH ₃ OH	" (100)	344
"	4-FC ₆ H ₄ C(CN)=CHC ₆ H ₅ (-)	344
"	4-ClC ₆ H ₄ C(CN)=CHC ₆ H ₅ (-)	344
C ₂ H ₅ OH	4-CH ₃ OC ₆ H ₄ CH=C(C ₆ H ₅)CN (88-100)	308
"	4-CH ₃ C ₆ H ₄ CH=C(C ₆ H ₅)CN (88-100)	308
"	3,4-(CH ₂ O ₂)C ₆ H ₃ CH=C(C ₆ H ₅)CN (88-100)	308
Xylene	C ₆ H ₅ C(C ₂ H ₅)=C(C ₆ H ₅)CN (-)	338
C ₂ H ₅ OH	C ₆ H ₅ C(CN)=CHC ₆ H ₄ N(CH ₃) ₂ -4 (85)	337
"	3-O ₂ NC ₆ H ₄ C(CN)=CHC ₆ H ₄ N(CH ₃) ₂ -4 (40)	337
"	4-O ₂ NC ₆ H ₄ C(CN)=CHC ₆ H ₄ N(CH ₃) ₂ -4 (95)	337
"	4-CH ₃ OC ₆ H ₄ C(C ₂ H ₅)=C(C ₆ H ₅)CN (-)	338
Xylene	1-C ₁₀ H ₇ CH=C(C ₆ H ₅)CN (88-100)	308

TABLE IV. ADDITION OF NITRILE-STABILIZED CARBANIONS TO

No. of C Atoms	Nucleophile	Electrophile	Base or Metal
C ₈ (Contd.)	C ₆ H ₅ CH ₂ CN	C ₆ H ₅ COC ₆ H ₅	<i>i</i> -C ₃ H ₇ MgBr
		9,9'-Bifluorenylidene	[C ₆ H ₅ CH ₂ N(CH ₃) ₃]OH
C ₉	C ₆ H ₅ CH(CH ₃)CN	HC≡CH	NaOH, [C ₆ H ₅ CH ₂ N(CH ₃) ₃]Cl, or [(C ₂ H ₅) ₄ N]Cl
		C ₂ H ₅ OC≡CH	NaOH, [C ₆ H ₅ CH ₂ N(CH ₃) ₃]Cl
	3-CH ₃ OC ₆ H ₄ CH ₂ CN		NaOC ₂ H ₅
	C ₆ H ₅ CH(CH ₃)CN	<i>n</i> -C ₄ H ₉ SC≡CH	NaOH, [C ₆ H ₅ CH ₂ N(CH ₃) ₃]Cl
	3-CH ₃ OC ₆ H ₄ CH ₂ CN		NaOC ₂ H ₅
	4-CH ₃ OC ₆ H ₄ CH ₂ CN	C ₆ H ₅ CHO	NaOH, polyethylene glycol
	"	"	NaOCH ₃
	"	2,6-Cl ₂ C ₆ H ₃ CHO	NaOH, polyethylene glycol
	"	4-CH ₃ OC ₆ H ₄ COC ₂ H ₅	NaNH ₂
	C ₁₀	C ₆ H ₅ CH(C ₂ H ₅)CN	HC≡CH
C ₆ H ₅ CHO			NaOH, polyethylene glycol
2,3-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN		"	NaOH
3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN		"	NaOC ₂ H ₅
3,5-(CH ₃) ₂ C ₆ H ₃ CH ₂ CN		"	"
3,5,4-(CH ₃) ₂ (O ₂ N)C ₆ H ₂ CH ₂ CN		"	"
C ₆ H ₅ CH(C ₂ H ₅)CN		C ₆ H ₅ C≡CH	NaOH, [C ₆ H ₅ CH ₂ N(CH ₃) ₃]Cl
3,5-(CH ₃) ₂ C ₆ H ₃ CH ₂ CN		4-(CH ₃) ₂ NC ₆ H ₄ CHO	NaOC ₂ H ₅
3,5,4-(CH ₃) ₂ (O ₂ N)C ₆ H ₂ CH ₂ CN		"	KOH
3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN		1-Benzyl-4-piperidone	NaOCH ₃
		NaNH ₂	

ALDEHYDES, KETONES, IMINES, ALKENES, AND ALKYNES (Continued)

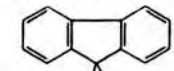


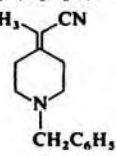
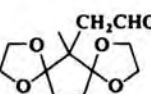
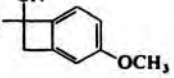
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₂ O	(C ₆ H ₅) ₂ COHCH(C ₆ H ₅)CN (40-63)	324
DMF	 CH(C ₆ H ₅)CN (82)	397
DMSO	C ₆ H ₅ C(CH=CH ₂)(CH ₃)CN (83)	90,89
"	C ₆ H ₅ C(CH ₃)(CN)C(OC ₂ H ₅)=CH ₂ (64)	88
C ₂ H ₅ OH	 C(C ₆ H ₄ OCH ₃ -3)CN (-)	339
DMSO	C ₆ H ₅ C(CH ₃)(CH=CHSC ₄ H ₉ - <i>n</i>)CN (74)	88
C ₂ H ₅ OH	 C(C ₆ H ₄ OCH ₃ -3)CN (-)	339
Toluene	C ₆ H ₅ CH=C(C ₆ H ₄ OCH ₃ -3)CN (59)	845
"	C ₆ H ₅ CH=C(C ₆ H ₄ OCH ₃ -4)CN (64)	845
CH ₃ OH	" (-)	344
Toluene	2,6-Cl ₂ C ₆ H ₃ CH=C(C ₆ H ₄ OCH ₃ -4)CN (55)	845
Xylene	4-CH ₃ OC ₆ H ₄ C(C ₂ H ₅)=C(C ₆ H ₄ OCH ₃ -4)CN (-)	338
DMSO	C ₆ H ₅ C(C ₂ H ₅)CH=CH ₂ CN (81)	89,90
Toluene	C ₆ H ₅ CH=C[C ₆ H ₃ (OCH ₃) ₂ -2,3]CN (69)	845
C ₂ H ₅ OH	3,4-(CH ₃ O) ₂ C ₆ H ₃ C(CN)=CHC ₆ H ₅ (88-100)	308
"	3,5-(CH ₃) ₂ C ₆ H ₃ C(CN)=CHC ₆ H ₅ (80)	337
"	3,5,4-(CH ₃) ₂ (O ₂ N)C ₆ H ₂ C(CN)=CHC ₆ H ₅ (90)	337
DMSO	C ₆ H ₅ C(CH=CHC ₆ H ₅)(C ₂ H ₅)CN (94)	90
"	3,5-(CH ₃) ₂ C ₆ H ₃ C(CN)=CHC ₆ H ₄ N(CH ₃) ₂ -4 (80)	337
C ₂ H ₅ OH	3,5,4-(CH ₃) ₂ (O ₂ N)C ₆ H ₂ C(CN)=CHC ₆ H ₄ N(CH ₃) ₂ -4 (90)	337
CH ₃ OH	3,4-(CH ₃ O) ₂ C ₆ H ₃  CN (-)	347
NH ₃	 CH ₂ CHOH  CN (66)	846

TABLE IV. ADDITION OF NITRILE-STABILIZED CARBANIONS TO

No. of C Atoms	Nucleophile	Electrophile	Base or Metal
C ₁₀ (Contd.)			NaNH ₂
C ₁₁	C ₆ H ₅ CH(C ₃ H _{7-i})CN C ₆ H ₅ CH(C ₃ H _{7-n})CN C ₆ H ₅ CH(C ₃ H _{7-i})CN	HC≡CH n-C ₄ H ₉ SC≡CH C ₆ H ₅ C≡CH	NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl " "
	ArCH ₂ CN	1-Benzyl-4-piperidone	NaOCH ₃ "
C ₁₂		XC ₆ H ₄ CHO	" KOH " " NaOCH ₃ " "
	1-C ₁₀ H ₇ CH ₂ CN	XC ₆ H ₄ CHO	NaOH KOH " " "
		C ₆ H ₅ CHO	NaNH ₂ "
	C ₆ H ₅ CH(C ₄ H _{9-n})CN 1-C ₁₀ H ₇ CH ₂ CN	C ₆ H ₅ C≡CH 4-CH ₃ OC ₆ H ₄ CHO 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO 4-(CH ₃) ₂ NC ₆ H ₄ CHO 3-O ₂ NC ₆ H ₄ COC ₃ H _{7-i}	" KOH " " NaNH ₂
	4- <i>t</i> -C ₄ H ₉ C ₆ H ₄ CH ₂ CN		"
C ₁₃	C ₆ H ₅ CH(C ₃ H _{11-n})CN	HC≡CH	NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
C ₁₄	(C ₆ H ₅) ₂ CHCN (<i>n</i> -C ₄ H ₉) ₃ SnCH ₂ CN (C ₆ H ₅) ₂ CHCN	(HCHO) ₆ CCl ₃ CHO C ₂ H ₅ OC≡CH n-C ₄ H ₉ SC≡CH	[C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]OH " NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl "

ALDEHYDES, KETONES, IMINES, ALKENES, AND ALKYNES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NH ₃ , THF	 (61)	174,175
DMSO	C ₆ H ₅ C(C ₃ H _{7-i})(CH=CH ₂)CN (82)	90
"	C ₆ H ₅ C(C ₃ H _{7-n})(CH=CHSC ₄ H _{9-n})CN (68)	88
"	C ₆ H ₅ C(C ₃ H _{7-i})(CH=CHSC ₄ H _{9-n})CN (74)	88
"	C ₆ H ₅ C(C ₃ H _{7-i})(CH=CHC ₆ H ₅)CN (83)	90
CH ₃ OH	 I Ar = 2,3,4-(CH ₃ O) ₃ C ₆ H ₂ (-) I Ar = 3,4,5-(CH ₃ O) ₃ C ₆ H ₂ (71)	347 347
"	 I X = H (-) I X = 2-Cl (-) I X = 3-Cl (-) I X = 4-Cl (-) I X = 4-OCH ₃ (-) I X = 2-NO ₂ (-) I X = 3-NO ₂ (-) I X = 4-N(CH ₃) ₂ (-)	345 345 345 345 345 345 345 345
C ₂ H ₅ OH	XC ₆ H ₄ CH=C(C ₁₀ H ₇₋₁)CN I I X = H (88-100) I X = Cl-2 (-) I X = NO ₂ -2 (-) I X = Cl-3 (-) I X = NO ₂ -3 (-) I X = Cl-4 (-)	308 847 847 847 847 847
(-)	 C(CN)(CHOHC ₆ H ₅)CH ₂ CH ₂ N(CH ₂) ₄ O (-)	568
NH ₃ C ₂ H ₅ OH	C ₆ H ₅ C(C ₄ H _{9-n})(CH=CHC ₆ H ₅)CN (96) 4-CH ₃ OC ₆ H ₄ CH=C(C ₁₀ H ₇₋₁)CN (-) 3,4-(CH ₂ O) ₂ C ₆ H ₃ CH=C(C ₁₀ H ₇₋₁)CN (-) 4-(CH ₃) ₂ NC ₆ H ₄ CH=C(C ₁₀ H ₇₋₁)CN (-)	89 847 847 847
Xylene	3-O ₂ NC ₆ H ₄ C(C ₃ H _{7-i})=C(C ₁₀ H ₇₋₁)CN (-)	338
"	 C(CH ₃)=C(CN)C ₆ H ₄ C ₄ H _{9-t-4} (-)	338
DMSO	C ₆ H ₅ C(C ₃ H _{11-n})(CH=CH ₂)CN (88)	90
Py	(C ₆ H ₅) ₂ C(CH ₂ OH)CN (94)	848
-	(<i>n</i> -C ₄ H ₉) ₃ SnOCH(CCl ₃)CH ₂ CN (-)	849
DMSO	(C ₆ H ₅) ₂ C(CN)C(OC ₂ H ₅)=CH ₂ (77)	88
"	(C ₆ H ₅) ₂ C(CH=CHSC ₄ H _{9-n})CN (55)	88

TABLE IV. ADDITION OF NITRILE-STABILIZED CARBANIONS TO

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₄ (Contd.)	(<i>n</i> -C ₄ H ₉) ₃ SnCH ₂ CN C ₆ H ₅ CH(CN)(CH ₂) ₂ N(C ₂ H ₅) ₂	C ₆ F ₃ CHO C ₆ H ₅ C≡CH	— NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
C ₁₅	C ₆ H ₅ CH ₂ CH(C ₆ H ₅)CN 4-ClC ₆ H ₄ CH ₂ CH(C ₆ H ₄ Cl-4)CN C ₆ H ₅ CH(CH ₂ C ₆ H ₅)CN (<i>Z</i>)-C ₆ H ₅ CH ₂ OCH ₂ CH=C(CH ₃)(CH ₂) ₂ CN C ₆ H ₅ CH(CH ₂ C ₆ H ₅)CN	(HCHO) _a " C ₂ H ₅ OC≡CH (CH ₃) ₂ CCHO <i>n</i> -C ₄ H ₉ SC≡CH C ₆ H ₅ C≡CH "	[C ₆ H ₅ CH ₂ N(CH ₃) ₃]OH " NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl LDA NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl " NaNH ₂ [C ₆ H ₅ CH ₂ N(CH ₃) ₃]OH NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
C ₁₆	(4-CH ₃ C ₆ H ₄) ₂ CHCN C ₆ H ₅ CH(CH ₃)CH(C ₆ H ₅)CN	(HCHO) _a <i>n</i> -C ₄ H ₉ SC≡CH	[C ₆ H ₅ CH ₂ N(CH ₃) ₃]OH NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
C ₁₇	4-CH ₃ OC ₆ H ₄ CH ₂ CH(C ₆ H ₄ OCH ₃ -4)CN	(HCHO) _a	[C ₆ H ₅ CH ₂ N(CH ₃) ₃]OH
C ₁₈	(1-C ₁₀ H ₇)CH(C ₆ H ₅)CN	"	"
C ₁₉	(1-C ₁₀ H ₇)CH ₂ CH(C ₆ H ₅)CN (1-C ₁₀ H ₇)CH(CH ₂ C ₆ H ₅)CN	" "	" "
C ₂₁	(C ₆ H ₅) ₂ CHCH(C ₆ H ₅)CN	(HCHO) _a C ₂ H ₅ OC≡CH <i>n</i> -C ₄ H ₉ SC≡CH	" NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl "

* The initial product was treated with (CH₃)₂SiCl.^ The initial product was reduced with LiAlH₄.

ALDEHYDES, KETONES, IMINES, ALKENES, AND ALKYNES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	(<i>n</i> -C ₄ H ₉) ₃ SnOCH(C ₆ F ₃)CH ₂ CN (—)	849
DMSO	C ₆ H ₅ C(CH=CHC ₆ H ₅)(CN)(CH ₂) ₂ N(C ₂ H ₅) ₂ (79)	90
Py	C ₆ H ₅ CH ₂ C(C ₆ H ₅)(CH ₂ OH)CN (93)	848
"	4-ClC ₆ H ₄ CH ₂ C(C ₆ H ₄ Cl-4)(CH ₂ OH)CN (44)	848
DMSO	C ₆ H ₅ C(CH ₂ C ₆ H ₅)(CN)(OC ₂ H ₅)=CH ₂ (74)	88
"	(<i>Z</i>)-C ₆ H ₅ CH ₂ OCH ₂ CH=C(CH ₃)(CH ₂) ₂ CH(CN)CHOHC ₄ H ₉ - <i>t</i> (—)	542
"	C ₆ H ₅ C(CH ₂ C ₆ H ₅)(CH=CHSC ₄ H ₉ - <i>n</i>)CN (78)	88
"	C ₆ H ₅ C(CH ₂ C ₆ H ₅)(CH=CHC ₆ H ₅)CN (98)	90
C ₆ H ₆	(—)	89
Py	(4-CH ₃ C ₆ H ₄) ₂ C(CH ₂ OH)CN (92)	848
DMSO	C ₆ H ₅ C(CH(CH ₃)C ₆ H ₅)(CH=CHSC ₄ H ₉ - <i>n</i>)CN (64)	88
Py	4-CH ₃ OC ₆ H ₄ CH ₂ C(C ₆ H ₄ OCH ₃ -4)(CH ₂ OH)CN (45)	848
"	1-C ₁₀ H ₇ C(C ₆ H ₅)(CH ₂ OH)CN (95)	848
"	1-C ₁₀ H ₇ CH ₂ C(C ₆ H ₅)(CH ₂ OH)CN (95)	848
"	1-C ₁₀ H ₇ C(CH ₂ C ₆ H ₅)(CH ₂ OH)CN (87)	848
"	(C ₆ H ₅) ₂ CHC(C ₆ H ₅)(CH ₂ OH)CN (91)	848
DMSO	C ₆ H ₅ C[CH(C ₆ H ₅) ₂][C(OC ₂ H ₅)=CH ₂]CN (100)	88
"	C ₆ H ₅ C[CH(C ₆ H ₅) ₂](CH=CHSC ₄ H ₉ - <i>n</i>)CN (96)	88

* The initial product was quenched with ceric ammonium nitrate.

^ The specific base was not identified.

TABLE V. TANDEM CONJUGATE ADDITION-ALKYLATION OF α,β -UNSATURATED NITRILES WITH CARBONYL COMPOUNDS





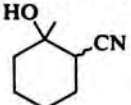




No. of C Atoms	Acceptor	Nucleophile	Electrophile	Metal	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₃	CH ₂ =CHCN	CH ₃ I	CH ₃ COCH ₃	Zn	CH ₃ CN	C ₂ H ₅ CH(CN)C(CH ₃) ₂ OH (52)	124	
		<i>i</i> -C ₃ H ₇ I	"	"	"	<i>i</i> -C ₄ H ₉ CH(CN)C(CH ₃) ₂ OH (98)	124	
		"	C ₂ H ₅ CHO	"	"	<i>i</i> -C ₄ H ₉ CH(CN)CH(C ₂ H ₅)OH (65)	124	
		<i>n</i> -C ₃ H ₇ I	CH ₃ COCH ₃	"	"	<i>n</i> -C ₄ H ₉ CH(CN)C(CH ₃) ₂ OH (63)	124	
		<i>i</i> -C ₃ H ₇ I	(CH ₃ CO) ₂ O	"	"	<i>i</i> -C ₄ H ₉ C(CN)=C(CH ₃)O ₂ CCH ₃ (81)	124	
		"		"	"	<i>t</i> -C ₄ H ₉ CH(CN)  (92)	124	
		"		"	"	<i>t</i> -C ₄ H ₉ CH(CN)  (99)	124	
		<i>i</i> -C ₃ H ₇ I	"	C ₆ H ₅ CHO	"	"	<i>i</i> -C ₄ H ₉ CH(CN)CH(OH)C ₆ H ₅ (94)	124
		"	C ₆ H ₁₁ I	CH ₃ COCH ₃	"	"	C ₆ H ₁₁ CH ₂ CH(CN)C(CH ₃) ₂ OH (95)	124
		"	C ₆ H ₅ CH ₂ Br	"	"	"	C ₆ H ₅ (CH ₂) ₂ CH(CN)C(CH ₃) ₂ OH (46)	124
		"	CH ₃ CO(CH ₂) ₃ I	"	"	"	 (42)	124
		C ₄	CH ₂ =C(CH ₃)CN CH ₃ CH=CHCN	<i>i</i> -C ₃ H ₇ I	CH ₃ COCH ₃	Zn	CH ₃ CN	<i>i</i> -C ₄ H ₉ C(CH ₃) ₂ (CN)C(CH ₃) ₂ OH (72)
"	C ₆ H ₅ CHO			"	"	<i>i</i> -C ₃ H ₇ CH(CH ₃)CH(CN)CH(C ₆ H ₅)OH (95)	124	
C ₁₅ -C ₁₇	CH ₂ =C(CH ₃)CN YC ₆ H ₄ CH=C(CN)C ₆ H ₄ Z	"	"	"	"	<i>i</i> -C ₄ H ₉ C(CH ₃) ₂ (CN)CH(C ₆ H ₅)OH (73)	124	
		RMgBr	R'X			YC ₆ H ₄ CHRC(CN)(R')C ₆ H ₄ Z I		
	Y = H, Z = H	R = CH ₃	R'X = CH ₃ I		Et ₂ O	I (88)	850	
	Y = H, Z = H	R = CH ₃	R'X = C ₂ H ₅ I		"	I (22)	850	
	Y = H, Z = H	R = CH ₃	R'X = C ₃ H ₇ Br- <i>n</i>		"	I (<i>threo</i> , 20; <i>erythro</i> , 72)	850	
	Y = H, Z = H	R = CH ₃	R'X = C ₅ H ₁₁ Br- <i>n</i>		"	I (18)	850	
	Y = H, Z = H	R = CH ₃	R'X = C ₅ H ₁₁ Br- <i>i</i>		"	I (18)	850	
	Y = H, Z = H	R = C ₂ H ₅	R'X = CH ₃ I		"	I (<i>threo</i> , —; <i>erythro</i> , 63)	850	
	Y = H, Z = H	R = C ₂ H ₅	R'X = C ₂ H ₅ I		"	I (—)	522	
	Y = H, Z = H	R = C ₂ H ₅	R'X = C ₃ H ₇ Br- <i>n</i>		"	I (20)	850	
	Y = H, Z = H	R = C ₂ H ₅	R'X = C ₅ H ₁₁ Br- <i>n</i>		"	I (20)	850	
	Y = H, Z = H	R = C ₂ H ₅	R'X = C ₅ H ₁₁ Br- <i>i</i>		"	I (90)	850	
	Y = H, Z = H	R = C ₃ H ₇ - <i>n</i>	R'X = CH ₃ I		"	I (50)	850	
	Y = H, Z = H	R = C ₃ H ₇ - <i>i</i>	R'X = CH ₃ I		"	I (18)	850	
	Y = H, Z = H	R = C ₃ H ₇ - <i>n</i>	R'X = C ₃ H ₇ Br- <i>n</i>		"	I (<i>threo</i> , 63; <i>erythro</i> , 23)	850	
	Y = H, Z = H	R = C ₄ H ₉ - <i>n</i>	R'X = CH ₃ I		"	I (13)	850	
	Y = H, Z = H	R = C ₅ H ₁₁ - <i>n</i>	R'X = CH ₃ I		"	I (13)	850	
	Y = OCH ₃ -4, Z = H	R = C ₂ H ₅	R'X = C ₂ H ₅ I		"	I (—)	851,850	
	Y = OCH ₃ -4, Z = OCH ₃ -4	R = C ₂ H ₅	R'X = C ₂ H ₅		"	I (—)	851	
	Y = OCH ₃ -4, Z = H	R = C ₂ H ₅	R'X = C ₃ H ₇ Br- <i>n</i>		"	I (47)	850	
	Y = H, Z = OCH ₃ -4	R = C ₂ H ₅	R'X = C ₂ H ₅ I		"	I (62)	850	
	Y = OCH ₃ -4, Z = OCH ₃ -4	R = CH ₃	R'X = CH ₃ I (50)		"	I (50)	850	

TABLE VI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₂	CH ₃ CN		<i>n</i> -C ₄ H ₉ Li
			"
			"
			"
		(<i>E</i>)-C ₆ H ₅ CH=CHSO ₂ CH ₃	LDA
		C ₆ H ₅ CH=CHCOCH ₃	<i>n</i> -C ₄ H ₉ Li or KN[Si(CH ₃) ₃] ₂
		CH ₃ CH=CHCOC ₆ H ₅	"
		(C ₆ H ₅) ₂ C=CHNO ₂	KF
		C ₆ H ₅ CH=CHCOC ₆ H ₅	<i>n</i> -C ₄ H ₉ Li or KN[Si(CH ₃) ₃] ₂
C ₃	C ₂ H ₅ CN	(<i>E</i>)-C ₆ H ₅ CH=CHSO ₂ CH ₃	LDA
C ₄	<i>i</i> -C ₃ H ₇ CN	"	"
	<i>n</i> -C ₃ H ₇ CN	"	"
C ₆	2-Thienylacetonitrile	CH ₂ =CHCO ₂ CH ₃	(CH ₃) ₄ NOH
C ₇	C ₆ H ₁₁ CN	CH ₃ CH=CHCHO	LiN(C ₂ H ₅) ₂
	2-Pyridylacetonitrile	CH ₂ =CHCO ₂ C ₂ H ₅	Na
	C ₆ H ₁₁ CN	C ₆ H ₅ CH=CHCHO	LiN(C ₂ H ₅) ₂

STABILIZED CARBANIONS TO VARIOUS MICHAEL ACCEPTORS

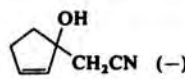
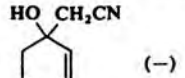
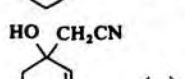
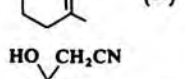
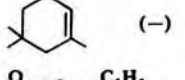
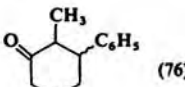
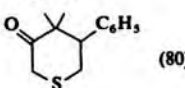
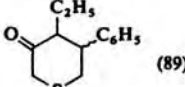
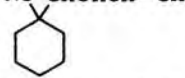
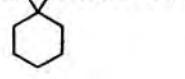


Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF, -80°	 (-)	369
"	 (-)	369
"	 (-)	369
"	 (-)	369
THF	 (51) [*]	391
THF, -80°	C ₆ H ₅ CH=CHCOH(CH ₃)CH ₂ CN (-)	369
"	CH ₃ CH=CHCOH(C ₆ H ₅)CH ₂ CN (-)	369
CH ₃ CN	O ₂ NCH ₂ C(C ₆ H ₅) ₂ CH ₂ CN (45)	392
THF, -80°	C ₆ H ₅ CH=CHCOH(C ₆ H ₅)CH ₂ CN (-)	369
THF	 (76) [*]	391
"	 (80) [*]	391
"	 (89) [*]	391
CH ₃ OH, <i>t</i> -C ₄ H ₉ OH	2-C ₄ H ₉ SCl[(CH ₂) ₂ CO ₂ CH ₃] ₂ CN (73) NC-CHOHCH=CHCH ₃	387,852
HMPA, C ₆ H ₆	 (70)	326
-	(2-C ₃ H ₄ N)CH(CN)CH ₂ CH ₂ CO ₂ C ₂ H ₅ (-) NC-CHOHCH=CHC ₆ H ₅	377
HMPA, C ₆ H ₆	 (65)	326

TABLE VI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₆	XC ₆ H ₄ CH ₂ CN	CH ₂ =CHCO ₂ CH ₃	(CH ₃) ₄ NOH
			"
C ₆ H ₅ CH ₂ CN	"	(E)-CH ₃ CH=CHCHO	"
			"
3-ClC ₆ H ₄ CH ₂ CN	"	"	n-C ₄ H ₉ Li
			"
C ₆ H ₅ CH ₂ CN	"	CH ₂ =C(CH ₃)CHO	"
			"
3-ClC ₆ H ₄ CH ₂ CN	"	"	"
			"
ArCH ₂ CN	"	CH ₂ =CHCO ₂ CH ₃	"
			[C ₆ H ₅ CH ₂ N(CH ₃) ₃]OH
C ₆ H ₅ CH ₂ CN	"	(CH ₃) ₂ C=CHCHO	"
			"
3-ClC ₆ H ₄ CH ₂ CN C ₆ H ₅ CH ₂ CN	"		"
			"
3-ClC ₆ H ₄ CH ₂ CN C ₆ H ₅ CH ₂ CN	"	CH ₂ =CHCO ₂ C ₂ H ₅ CH ₃ CH=CHCO ₂ CH ₃ CH ₂ =C(CH ₃)CO ₂ CH ₃ (CH ₃) ₂ C=CHCHO (CH ₃) ₂ C=CHCOCH ₃	LDA Cu ₂ O. C ₆ H ₁₁ NC LDA "
			n-C ₄ H ₉ Li
3-ClC ₆ H ₄ CH ₂ CN	"		"
			"
3-ClC ₆ H ₄ CH ₂ CN	"	CH ₃ CH=CHCO ₂ C ₂ H ₅ (CH ₃) ₂ C=CHCOCH ₃	n-C ₄ H ₉ Li " " LDA

STABILIZED CARBANIONS TO VARIOUS MICHAEL ACCEPTORS (Continued)








Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
CH ₃ OH, <i>t</i> -C ₄ H ₉ OH	XC ₆ H ₄ C[(CH ₂) ₂ CO ₂ CH ₃] ₂ CN I	387
"	I X = H (70)	387
"	I X = Br-4 (70)	387
"	I X = Cl-3 (64)	387
"	I X = Cl ₂ -3,4 (70)	387
"	I X = Cl ₂ -2,4 (67)	387
1:4 HMPA:THF, -70°. 30 min	CH ₃ CH=CHCHOHCH(C ₆ H ₅)CN I, C ₆ H ₅ CH(CN)CH(CH ₃)CH ₂ CHO II	365
THF, -70°. 30 min. and 0 to -30°, 2-3 hr	I:II = 65:35 (75) I:II = 0:100 (60)	367
1:4 HMPA:THF, -70°. 30 min	CH ₃ CH=CHCHOHCH(C ₆ H ₄ Cl-3)CN I, 3-ClC ₆ H ₄ CH(CN)CH(CH ₃)CH ₂ CHO II	365
THF, -70°. 30 min. and 0 to -30°, 2-3 hr	I:II = 35:65 (55) I:II = 0:100 (70)	367
1:4 HMPA:THF, -70°. 30 min	CH ₂ =C(CH ₃)CHOHCH(C ₆ H ₅)CN I, C ₆ H ₅ CH(CN)CH ₂ CH(CH ₃)CHO II	365
THF, -70°. 30 min. and 0 to -30°, 2-3 hr	I:II = 25:75 (80) I:II = 0:100 (75)	367
1:4 HMPA:THF, -70°. 30 min	CH ₂ =C(CH ₃)CHOHCH(C ₆ H ₄ Cl-3)CN I, 3-ClC ₆ H ₄ CH(CN)CH ₂ CH(CH ₃)CHO II	365
THF, -70°. 30 min. and 0 to -30°, 2-3 hr	I:II = 15:85 (80) I:II = 0:100 (75)	367
CH ₃ OH, <i>t</i> -C ₄ H ₉ OH	ArC(CN)[(CH ₂) ₂ CO ₂ CH ₃] ₂ I	383,387
"	I Ar = C ₆ H ₄ Cl-4 (71)	383,387
"	I Ar = C ₆ H ₄ F-4 (72)	387
"	I Ar = C ₆ H ₄ Cl-2 (73)	387
1:4 HMPA:THF, -70°. 30 min	(CH ₃) ₂ C=CHCHOHCH(C ₆ H ₅)CN I, C ₆ H ₅ CH(CN)C(CH ₃) ₂ CH ₂ CHO II	365
THF, -70°, 30 min, and 0 to -30°, 2-3 hr	I:II = 75:25 (90) I:II = 0:100 (65)	367
THF, -70°, 10 min	 (90)	369
THF, -78°	CH(C ₆ H ₅)CN	
—	C ₆ H ₅ CH(CN)(CH ₂) ₂ CO ₂ C ₂ H ₅ (50)	386,389
THF, -78°	C ₆ H ₅ CH(CN)CH(CH ₃)CH ₂ CO ₂ CH ₃ (53)	381
THF, -70°. 30 min, and 0 to -30°, 2-3 hr	C ₆ H ₅ CH(CN)CH ₂ CH(CH ₃)CO ₂ CH ₃ (40)	389
THF or DME, -70°	3-ClC ₆ H ₄ CH(CN)C(CH ₃) ₂ CH ₂ CHO (85)	367
THF or DME, ZnCl ₂ , -70°	(CH ₃) ₂ C=CHC(CH ₃)OHCH(CN)C ₆ H ₅ I, (CH ₃) ₂ C[CH(CN)C ₆ H ₅]CH ₂ COCH ₃ II	376
	I:II = 5:95 (-) I:II = 95:5 (-)	
THF, -70°, 1 min	 CH(C ₆ H ₅)CN	
THF, -70°, 15 min	I:II = 55:45 (65)	369,370
THF, -60°, 3 hr	I:II = 70:30 (70)	369,370
THF, -78°	I:II = 100:0 (90)	369,383
	C ₆ H ₅ CH(CN)CH(CH ₃)CH ₂ CO ₂ C ₂ H ₅ (90)	389,386
	(CH ₃) ₂ C=CHCOH(CH ₃)CH(CN)C ₆ H ₄ Cl-3 I, (CH ₃) ₂ C[CH(CN)C ₆ H ₄ Cl-3]CH ₂ COCH ₃ II	

TABLE VI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₆ (Contd.)	3-ClC ₆ H ₄ CH ₂ CN	(CH ₃) ₂ C=CHCOCH ₃	n-C ₄ H ₉ Li
			"
C ₆ H ₅ CH ₂ CN	C ₆ H ₅ CH ₂ CN	"	"
			"
		"	"
		"	"
			"
		CH ₃ CH=CHCH=NC ₆ H _{9-t}	"
			"
3-ClC ₆ H ₄ CH ₂ CN	3-ClC ₆ H ₄ CH ₂ CN	CH ₃ CH=CHCH=NC ₆ H _{9-t}	"
			"
C ₆ H ₅ CH ₂ CN	C ₆ H ₅ CH ₂ CN	C ₆ H ₅ CH=CHCHO	"
		(CH ₃) ₂ C=CHCH=NC ₆ H _{9-t}	"

STABILIZED CARBANIONS TO VARIOUS MICHAEL ACCEPTORS (Continued)

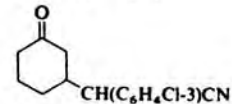
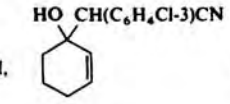
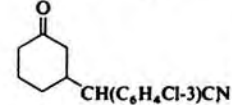

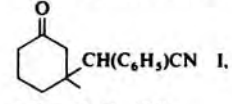
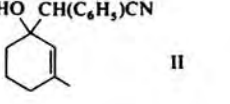
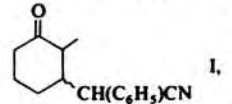
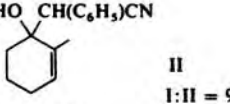
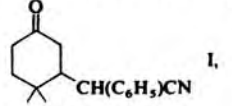
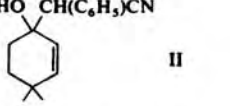
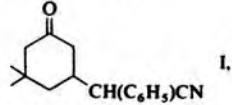
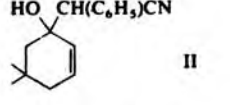
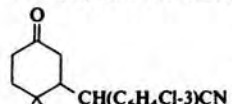
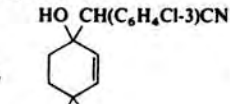

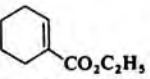
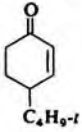
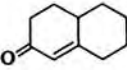
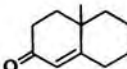
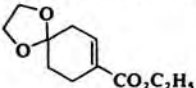
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF or DME. -70°	1:II = 5:95 (-)	376
THF or DME. ZnCl ₂ . -70°	1:II = 95:5 (-)	376
THF. -90°	 I,  II	853
	1:II = 90:10 (75)	
1:4 HMPA:THF	 I,  II	854
	(>95)	
THF. -90°. 2 min	 I,  II	369,370
THF. -70°. 15 min	1:II = 35:65 (70)	369,853
THF. -60°. 2 hr	1:II = 70:30 (75)	369
	1:II = 100:0 (95)	369
THF. -90°	 I,  II	853
	1:II = 95:5 (80)	
1:4 HMPA:THF. -70°	C ₆ H ₅ CH(CN)CH(CH ₃)CH ₂ CHO (80)*	367
THF. -30°	 I,  II	853
	1:II = 95:5 (70)	
THF. -90°	 I,  II	853
	1:II = 95:5 (95)	
1:4 HMPA:THF. -70°	3-ClC ₆ H ₄ CH(CN)CH(CH ₃)CH ₂ CHO (70)*	367
THF. -50°	 I,  II	853
	1:II = 95:5 (50)	
1:4 HMPA:THF. -70°. 30 min	C ₆ H ₅ CH=CHCHOHCH(C ₆ H ₅)CN I,	365
THF. -70°, 30 min, and 0 to -30°. 2-3 hr	C ₆ H ₅ CH(CN)CH(C ₆ H ₅)CH ₂ CHO II	367
1:4 HMPA:THF. -70°	1:II = 65:35 (73)	367
	1:II = 0:100 (60)	367
	C ₆ H ₅ CH(CN)C(CH ₃) ₂ CH ₂ CHO (10)*	367

TABLE VI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₆ (Contd.)	C ₆ H ₅ CH ₂ CN		<i>n</i> -C ₄ H ₉ Li
		"	"
	3-ClC ₆ H ₄ CH ₂ CN		LDA
		C ₆ H ₅ CH=CHCHO	"
	C ₆ H ₅ CH ₂ CN	"	<i>n</i> -C ₄ H ₉ Li
		C ₆ H ₅ CH=CHCOCH ₃	NaOCH ₃ <i>n</i> -C ₄ H ₉ Li
	"	"	"
	"	"	"
	"	CH ₃ CH=CHCOC ₆ H ₅	NaOCH ₃ <i>n</i> -C ₄ H ₉ Li
	"		"
"		"	
4-XC ₆ H ₄ CH ₂ CN	C ₆ H ₅ CH=CHCO ₂ CH ₃	NaOCH ₃	
C ₆ H ₅ CH ₂ CN		"	
	(<i>E</i>)-C ₆ H ₅ CH=CHCO ₂ C ₂ H ₅	LDA	
"		"	

STABILIZED CARBANIONS TO VARIOUS MICHAEL ACCEPTORS (Continued)

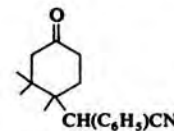
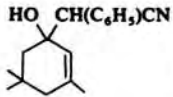
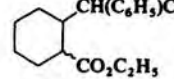
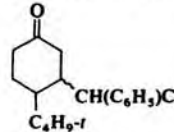
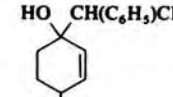

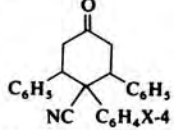

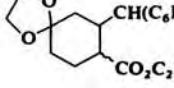
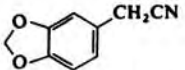


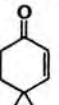

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF, -70°	 I,  II CH(C ₆ H ₅)CN	853
THF, -70°, 15 min	I:II = 95:5 (95)	369,370
THF, -78°	I (95)  CH(C ₆ H ₅)CN (73)	386,389
THF, -70°, 30 min, and 0 to -30°, 2-3 hr CH ₃ OH	C ₆ H ₅ CH=CHCHOHCH(C ₆ H ₄ Cl-3)CN I, 3-ClC ₆ H ₄ CH(CN)CH(C ₆ H ₅)CH ₂ CHO II	367
THF, -70°, 1 min	I:II = 0:100 (70) II (10)	367
THF, -70°, 15 min	C ₆ H ₅ CH=CHCOH(CH ₃)CH(C ₆ H ₅)CN I, C ₆ H ₅ CH(CN)CH(C ₆ H ₅)CH ₂ COCH ₃ II	369,370
THF, -60°, 2 hr CH ₃ OH, 0°	I:II = 78:22 (70)	369,370
THF, -90°, 2 min	I:II = 28:72 (85) II (70: <i>erythro:threo</i> = 65:35) C ₆ H ₅ CH(CN)CH(CH ₃)CH ₂ COC ₆ H ₅ (85)	373 369,370
THF, -70°	 I,  II CH(C ₆ H ₅)CN	853
THF, HMPA, THF, -45° THF, HMPA, -40° THF, -45°	I:II = 80:20 (80) I (60),  II CH(C ₆ H ₅)CN	855 855 855 855
Toluene	I:II = 2:3 (60)	
"	I:II = 2:3 (90) I (60)	
THF, -30°	I (90)	
THF, -78°	 I C ₆ H ₅ CH(CN)CH(C ₆ H ₅)CH ₂ CO ₂ CH ₃ (74)	856 856
"	I X = H (45) I X = Cl (53)	
"	 (90) CH(C ₆ H ₅)CN	855
"	C ₆ H ₅ CH(CN)CH(C ₆ H ₅)CH ₂ CO ₂ C ₂ H ₅ (74)	386,389
"	 CH(C ₆ H ₅)CN (73)	386,389

TABLE VI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₉ (Contd.)	4-CH ₃ OC ₆ H ₄ CH ₂ CN	(CH ₃) ₂ C=CHCHO	n-C ₄ H ₉ Li
		CH ₂ =CHCO ₂ C ₂ H ₅	[C ₆ H ₅ CH ₂ N(CH ₃) ₃]OH
	2-(2-Pyridyl)butyronitrile C ₆ H ₅ CH(CH ₃)CN 4-CH ₃ OC ₆ H ₄ CH ₂ CN	CH ₂ =CHCO ₂ C ₂ H ₅ HOCH ₂ C(CH ₃) ₂ COCH ₃ (CH ₃) ₂ C=CHCOCH ₃	Na KOCH ₃
			n-C ₄ H ₉ Li
		"	"
			"
		"	"
		CH ₃ CH=CHCH=NC ₆ H ₅ - <i>l</i>	"
			"
			"

STABILIZED CARBANIONS TO VARIOUS MICHAEL ACCEPTORS (Continued)

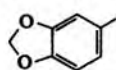
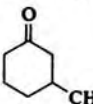

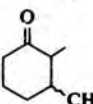

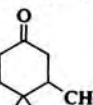

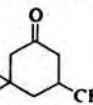


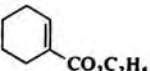
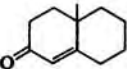
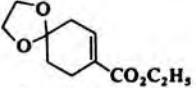
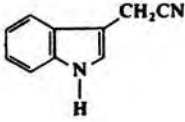
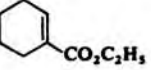
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
1:4 HMPA:THF, -70°, 30 min THF, -70°, 30 min, and 0 to -30°, 2-3 hr	4-CH ₃ OC ₆ H ₄ CH(CN)CHOHCH=C(CH ₃) ₂ I, 4-CH ₃ OC ₆ H ₄ CH(CN)C(CH ₃) ₂ CH ₂ CHO II I:II = >95:5 (≥95) I:II = 0:100 (80)	365 367
CH ₃ CN	 (100)	860
—	2-C ₅ H ₄ NC(C ₂ H ₅)(CN)(CH ₃) ₂ CO ₂ C ₂ H ₅ (-)	377
—	C ₆ H ₅ C(CH ₃)(CN)(CH ₂) ₂ COC ₃ H ₇ - <i>i</i> (8) (CH ₃) ₂ C=CHCOH(CH ₃)CH(CN)C ₆ H ₄ OCH ₃ -4 I, (CH ₃) ₂ C[CH(CN)C ₆ H ₄ OCH ₃ -4]CH ₂ COCH ₃ II	253
THF or DME, -70° THF or DME, ZnCl ₂ , -70°	I:II = 5:95 (-) I:II = 95:5 (-)	376 376
THF, -40°	 I, HO-CH(C ₆ H ₄ OCH ₃ -4)CN  II.	853
1:4 THF:HMPA	I:II = 95:5 (80) I (>95)	854
THF, 90°	 I, HO-CH(C ₆ H ₄ OCH ₃ -4)CN  II	853
1:4 HMPA:THF 1:4 HMPA:THF, -70°	I:II = 90:10 (95) I (>95) 4-CH ₃ OC ₆ H ₄ CH(CN)CH(CH ₃)CH ₂ CHO (90) ^a	854 367
THF, -20°	 I, HO-CH(C ₆ H ₄ OCH ₃ -4)CN  II	853
THF, -40°	I:II = 95:5 (80)  I, HO-CH(C ₆ H ₄ OCH ₃ -4)CN  II	861
	I:II = 95:5 (80)	

TABLE VI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₉ (Contd.)	4-CH ₃ OC ₆ H ₄ CH ₂ CN	C ₆ H ₅ CH=CHCHO	<i>n</i> -C ₄ H ₉ Li
			"
			"
		(CH ₃) ₂ C=CHCH=NC ₄ H ₉ - <i>t</i>	"
			"
		"	"
	2-CH ₃ OC ₆ H ₄ CH ₂ CN		LDA
	C ₆ H ₅ CH(CH ₃)CN	(<i>E</i>)-C ₆ H ₅ CH=CHCOCH ₃	NaOCH ₃
	4-CH ₃ OC ₆ H ₄ CH ₂ CN		<i>n</i> -C ₄ H ₉ Li
	2-CH ₃ OC ₆ H ₄ CH ₂ CN		NaH
	3-CH ₃ OC ₆ H ₄ CH ₂ CN	"	"
C ₁₀	4-CH ₃ OC ₆ H ₄ CH ₂ CN	C ₆ H ₅ CH=CHCH=NC ₄ H ₉ - <i>t</i>	<i>n</i> -C ₄ H ₉ Li
	C ₆ H ₅ C(CN)=CHCH ₃	CH ₂ =CHCN	[C ₆ H ₅ CH ₂ N(CH ₃) ₂]OH
	3-CH ₃ OC ₆ H ₄ CH(CH ₃)CN	"	"
	C ₆ D ₂ CD(C ₂ H ₅)CN	CH ₂ =CHCO ₂ CH ₃	"
	3-CH ₃ OC ₆ H ₄ CH(CH ₃)CN	"	"
	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN	"	(CH ₃) ₄ NOH
	2,5-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN	CH ₃ CH=CHCO ₂ C ₂ H ₅	LDA
		[(CH ₃) ₂ N=CHC(X)=CHN(CH ₃) ₂]ClO ₄	NaOCH ₃
		"	"
	2,5-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN		LDA

STABILIZED CARBANIONS TO VARIOUS MICHAEL ACCEPTORS (Continued)



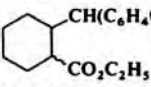
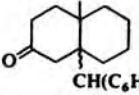
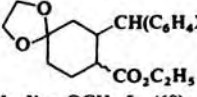
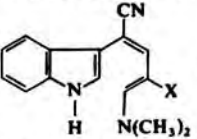
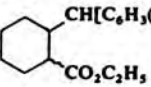
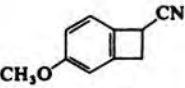
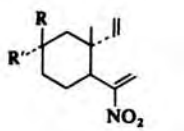
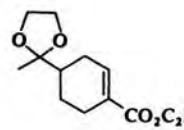
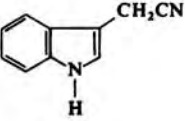
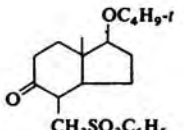
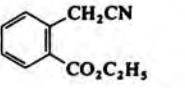
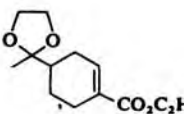
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	C ₆ H ₅ CH=CHCHOHCH(C ₆ H ₄ OCH ₃ -4)CN I, 4-CH ₃ OC ₆ H ₄ CH(CN)CH(C ₆ H ₅)CH ₂ CHO II	
1:4 HMPA:THF, -70°, 30 min	1:II = 70:30 (85)	365
THF, -78°	1:II = 100:0 (80)	366
THF, -70°, 30 min, and 0 to -30°, 2-3 hr	1:II = 0:100 (70)	367
THF, HMPA, -78°	1:II = 1:1 (80)	862
THF, -78°	I (80)	862
1:4 HMPA:THF, -70°	4-CH ₃ OC ₆ H ₄ CH(CN)C(CH ₃) ₂ CH ₂ CHO (30)*	367
		I,
THF, -70°		853
		II
	1:II = 95:5 (80)	
1:4 HMPA:THF	I (>95)	854
		(76)
THF		386,389
CH ₃ OH, 0°	C ₆ H ₅ C(CH ₃)(CN)CH(C ₆ H ₅)CH ₂ COCH ₃ <i>erythro</i> (83), <i>threo</i> (17)	374
		(90)
THF, -30°		355
		I, X = OCH ₃ -2 (73)
THF, -45°		389
	I X = OCH ₃ -3 (68)	389
	4-CH ₃ OC ₆ H ₄ CH(CN)CH(C ₆ H ₅)CH ₂ CHO (70)*	367
1:4 HMPA:THF, -70°		
Aq <i>t</i> -C ₄ H ₉ OH	C ₆ H ₅ C(CH=CH ₂)(CN)(CH ₂) ₂ CN (-)	341
Dioxane	3-CH ₃ OC ₆ H ₄ C(CH ₃)(CN)(CH ₂) ₂ CN (58)	378
"	C ₆ D ₂ C(C ₂ H ₅)(CN)(CH ₂) ₂ CO ₂ CH ₃ (80)	385
"	3-CH ₃ OC ₆ H ₄ C(CH ₃)(CN)(CH ₂) ₂ CO ₂ CH ₃ (63)	380,378
CH ₃ OH or dioxane	3,4-(CH ₃ O) ₂ C ₆ H ₃ C(CN)[(CH ₂) ₂ CO ₂ CH ₃] ₂ (65)	387
CH ₃ OH, <i>t</i> -C ₄ H ₉ OH	2,5-(CH ₃ O) ₂ C ₆ H ₃ CH(CN)CH(CH ₃)CH ₂ CO ₂ C ₂ H ₅ (89)	389
THF, -78°		
		I, X = H (-)
		359
	I X = OCH ₃ (-)	359
		(52)
THF, -78°		389,863

TABLE VI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₀ (Contd.)			NaNH ₂
			"
	2,5-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN		LDA
		[(CH ₃) ₂ N=CHC(C ₆ H ₅)=CHN(CH ₃) ₂] ₂ ClO ₄	NaOCH ₃
	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN		KH
C ₁₁	3-CH ₃ OC ₆ H ₄ CH(C ₂ H ₅)CN	CH ₂ =CHCO ₂ CH ₃	[C ₆ H ₅ CH ₂ N(CH ₃) ₂]OH
		RC≡CCO ₂ C ₂ H ₅	NaH
C ₁₂	4- <i>t</i> -C ₄ H ₉ C ₆ H ₄ CH ₂ CN 1-Naphthylacetonitrile	CH ₂ =CHCO ₂ CH ₃	(CH ₃) ₄ NOH [C ₆ H ₅ CH ₂ N(CH ₃) ₂]OH
		[(CH ₃) ₂ N=CHC(X)=CHN(CH ₃) ₂] ₂ ClO ₄	NaOCH ₃
		"	"
	2-Naphthylacetonitrile		LDA

STABILIZED CARBANIONS TO VARIOUS MICHAEL ACCEPTORS (Continued)

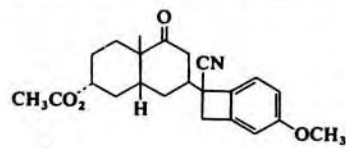
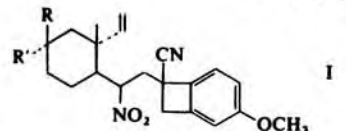
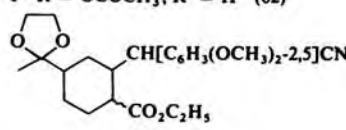
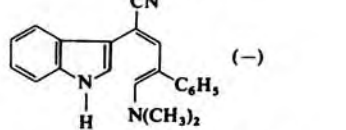
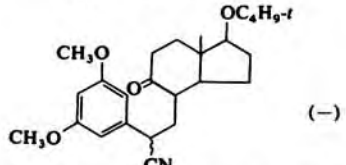
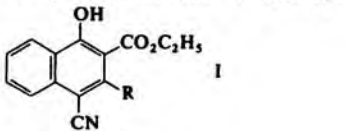
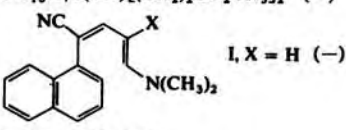
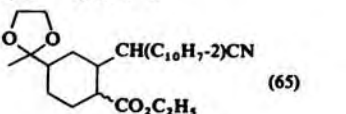
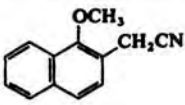
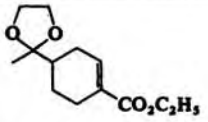
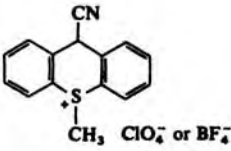
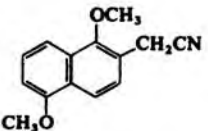
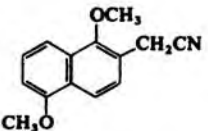
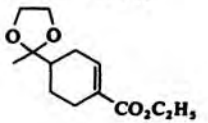
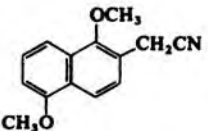
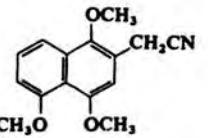
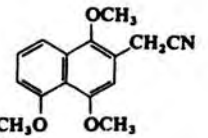
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NH ₃ , -78°	 (-)	395
"	 I	175,394 393,394
"	I R, R' = O(CH ₂) ₂ O (72) I R = OCOCH ₃ , R' = H (62)	
THF, -20°	 (64)	386,389
-	 (-)	359
Toluene	 (-)	864
Dioxane	3-CH ₃ OC ₆ H ₄ C(C ₂ H ₅)(CN)(CH ₂) ₂ CO ₂ CH ₃ (34)	378
DME	 I	865
	I R = H (80) I R = CH ₃ (95) I R = CO ₂ C ₂ H ₅ (30)	
CH ₃ OH, <i>t</i> -C ₄ H ₉ OH	4- <i>t</i> -C ₄ H ₉ C ₆ H ₄ C(CN)[(CH ₂) ₂ CO ₂ CH ₃] ₂ (59)	387
<i>t</i> -C ₄ H ₉ OH	1-C ₁₀ H ₇ C(CN)[(CH ₂) ₂ CO ₂ CH ₃] ₂ (-)	383
-	 I, X = H (-)	359
-	I, X = C ₆ H ₅ (-)	359
THF, -78°	 (65)	389

TABLE VI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₃			NaH
C ₁₄	(C ₆ H ₅) ₂ CHCN	(CH ₃) ₂ C(Br)CO ₂ C ₂ H ₅ BrCH ₂ CH(CH ₃)CO ₂ C ₂ H ₅ (CH ₃) ₂ CBrCO ₂ C ₂ H ₅	NaOC ₂ H ₅ NaNH ₂ NaOC ₂ H ₅
		CH ₃ O ₂ CC≡CCO ₂ CH ₃	NaH
		(NC) ₂ C=C(CN) ₂	"
			KH
		"	NaH
C ₁₅		"	"
		"	KH
	9-Phenanthrylacetonitrile	[(CH ₃) ₂ N=CHC(C ₆ H ₅)=CHN(CH ₃) ₂] ₂ ClO ₄	NaOCH ₃

* The initial product was hydrolyzed with aqueous acid.

STABILIZED CARBANIONS TO VARIOUS MICHAEL ACCEPTORS (Continued)

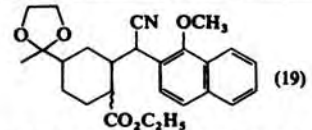
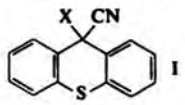
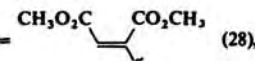

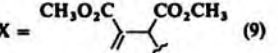
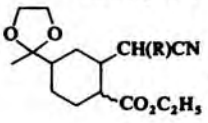
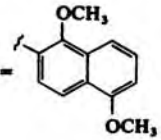
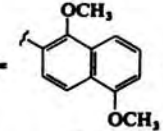
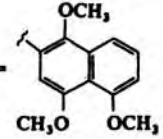
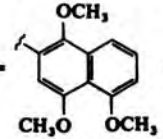
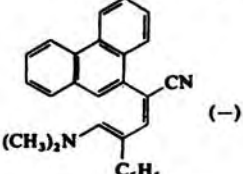
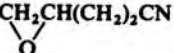
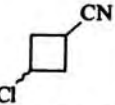
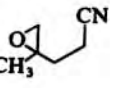
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF, -45°	 (19)	389
C ₂ H ₅ OH	(C ₆ H ₅) ₂ C(CN)CH ₂ CH(CH ₃)CO ₂ C ₂ H ₅ (85-90 crude)	252
C ₆ H ₆	" (-)	252
C ₂ H ₅ OH	(C ₆ H ₅) ₂ C(CN)CH ₂ CH(CH ₃)CO ₂ C ₂ H ₅ (90)	794
C ₆ H ₆	 I I X =  (28), I X =  (4), I X =  (9)	52
THF	I X = CH(CN) ₂ (11)	52
THF, -20°	 I, R =  (79)	389,390
-	I, R =  (-)	866
THF, 0°	I, R =  (94)	388
THF, -20°	I, R =  (72)	389,390
	 (-)	359

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₂	CH ₃ CN	Br(CH ₂) _n Br
		Cl(CH ₂) ₅ Cl
		[BrCH ₂ Si(CH ₃) ₂] ₂ O
C ₃	C ₂ H ₅ CN	"
C ₄	Cl(CH ₂) ₃ CN	—
		—
		—
		—
C ₅		—
	Cl(CH ₂) ₄ CN	—
		—
	CH ₃ CCl(NO ₂)(CH ₂) ₂ CN	—
C ₆		—
	Cl(CH ₂) ₃ CH(CH ₃)CN	—
	C ₂ H ₅ CCl(NO ₂)(CH ₂) ₂ CN	—
	NC(CH ₂) ₄ CN	—

NITRILE-STABILIZED CARBANIONS

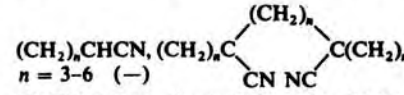
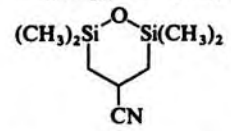
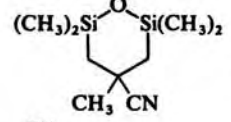
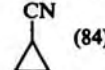
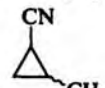
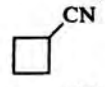
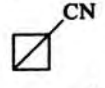
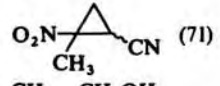
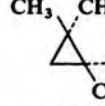
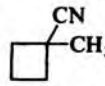
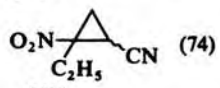
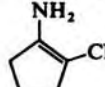
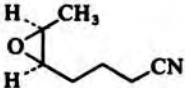
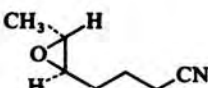
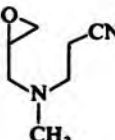
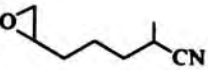
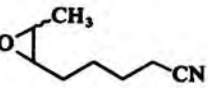

Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NaN[Si(CH ₃) ₃] ₂	Et ₂ O, -60°	(CH ₂) _n CHCN, (CH ₂) _n C  (n = 3-6) (-)	105
NaNH ₂		NC(CH ₂) ₇ CN (low), C ₆ H ₁₁ CN (high)	209
NaN[Si(CH ₃) ₃] ₂	C ₆ H ₆ , toluene	(CH ₃) ₂ Si  Si(CH ₃) ₂ (-)	218
"	"	(CH ₃) ₂ Si  Si(CH ₃) ₂ (-)	218
NaH	HMPA	 (84)	187
NaNH ₂	"	" (54)	187
—	"	" (-)	185
NaNH ₂	NH ₃	" (53)	543
LDA	—	 (59)	220
LiN(C ₂ H ₅) ₂	HMPA	 (62)	193
<i>t</i> -C ₄ H ₉ OK	<i>t</i> -C ₄ H ₉ OH	 (8-11)	129b
50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	CH ₃ CN	 (71)	867
KNH ₂	NH ₃ , DME	 (-)	222,221
LiN(C ₂ H ₅) ₂	HMPA	 (61)	193
50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	CH ₃ CN	 (74)	867
KH	THF	 (79-88)	868

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₆ (Contd.)	2-Furylacetonitrile	Br(CH ₂) ₃ Br
	2-Thienylacetonitrile	"
C ₇		—
		—
	Cl(CH ₂) ₃ CH(C ₂ H ₅)CN	—
		—
	NC(CH ₂) ₅ CN	—
C ₈		—
		—
		—

NITRILE-STABILIZED CARBANIONS (Continued)





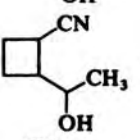
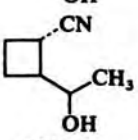
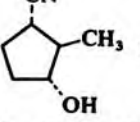
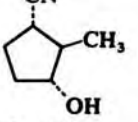

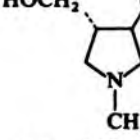
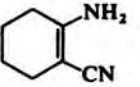
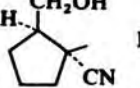
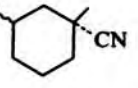
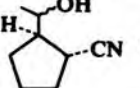

Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NaH	DMSO	 -C ₄ H ₃ O-2 (58)	204
"	"	 -C ₄ H ₃ S-2 (58)	204
NaNH ₂	THF, 40°	 (—),  (—)	224
"	"	 I,  II,	
		 III,  IV	224
		I + II:III + IV = 28:72 (90)	
LiN(C ₂ H ₅) ₂	HMPA	 -C ₂ H ₅ (82)	193
NaN[Si(CH ₃) ₃] ₂	C ₆ H ₆	 (63-67)	225
KH	THF	 -NH ₂ (83)	868
KNH ₂	NH ₃ , DME	 I,  II	221
		I:II = 1:2 (86)	
"	"	 (77)	223,221
KN[Si(CH ₃) ₃] ₂	C ₆ H ₆ , 80°	 -C(CH ₃) ₂ OH (70)	222

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₈ (Contd.)	Cl(CH ₂) ₃ CH(C ₃ H _{7-i})CN	—
	Cl(CH ₂) ₄ CH(C ₂ H ₅)CN	—
C ₆ H ₅ CH ₂ CN	Br(CH ₂) ₂ Br	
	Cl(CH ₂) ₂ Cl	
	CH ₃ OCH ₂ Cl	
XC ₆ H ₄ CH ₂ CN	Br(CH ₂) ₃ Br	
	Cl(CH ₂) ₃ Cl	
C ₆ H ₅ CH ₂ CN	CH ₃ CH(Br)CH ₂ Br	
	Br(CH ₂) ₄ Br	
	"	
	"	
	"	
	"	
	"	
	CH ₃ CHBr(CH ₂) ₂ Br	
	Cl(CH ₂) ₄ Cl	

NITRILE-STABILIZED CARBANIONS (Continued)

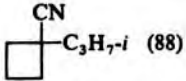
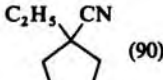
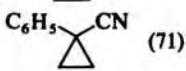
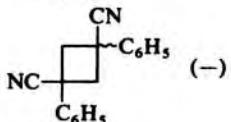
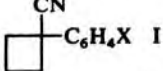
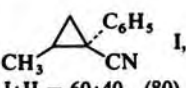
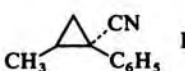
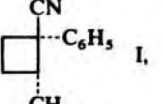
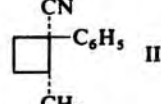
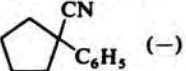
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
LiN(C ₂ H ₅) ₂	HMPA	 (88)	193
"	"	 (90)	193
"	"	 (71)	186,102,184
n-C ₄ H ₉ Li	THF, 25°	" (65)	47,46
NaNH ₂	Et ₂ O	 (-)	869
NaH	DMSO	 I I X = H (58) I X = Cl-2 (75) I X = Cl-3 (53) I X = Cl-4 (78) I X = Br-2 (60) I X = F-2 (40) I X = Cl ₂ -2,6 (65) I X = H (41) I X = H (26)	204
n-C ₄ H ₉ Li 50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	THF, 25°		47 70
NaNH ₂	Toluene, 110°	 I, I:II = 60:40 (80)	190
NaOH	—	 II	199,197
KOH	DMF	" (68)	203
NaH	DMSO	" (72)	204
C ₁₀ H ₈ Na	THF	" (63)	198
NaNH ₂	Toluene	" (70)	196
"	C ₆ H ₆ , 80°	 I, I:II = 86:14 (72)	190
		 II	
50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	—	 (-)	71,870

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile _s	Electrophile
C ₈ (Contd.)	C ₆ H ₅ CH ₂ CN	Cl(CH ₂) ₄ Cl
		Br(CH ₂) ₄ Br
		"
	4-ClC ₆ H ₄ CH ₂ CN	Cl(CH ₂) ₄ Cl
		Br(CH ₂) ₄ Br
	C ₆ H ₅ CH ₂ CN	Br(CH ₂) ₃ Br
		"
		"
		"
		CH ₃ CHBr(CH ₂) ₃ Br
2-FC ₆ H ₄ CH ₂ CN	CH ₃ N[(CH ₂) ₂ Cl] ₂	

NITRILE-STABILIZED CARBANIONS (Continued)

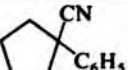
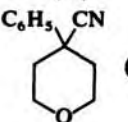
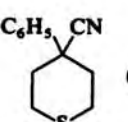
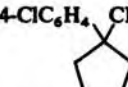
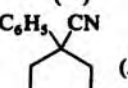
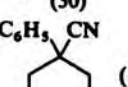
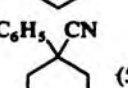
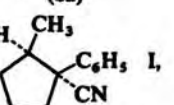
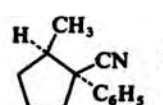
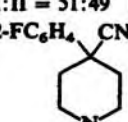
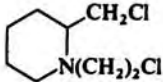
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NaNH ₂	Toluene	 (79)	195
50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	"	" (88)	70,85
<i>n</i> -C ₄ H ₉ Li	THF, 25°	" (47)	47
NaOH	DMSO	" (82)	871,872
NaOH. (C ₂ H ₅) ₄ NOH	<i>n</i> -C ₃ H ₇ OH	 (68)	201,202
50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	"	" (-)	70
NaNH ₂	"	 (40)	211
"	Toluene	 (-)	195
NaOH	-	" (-)	200
NaH	DMSO	 (54)	204
NaOH	-	" (30)	199
50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	-	 (-), C ₆ H ₅ CH(CN)(CH ₂) ₃ Br (-)	70
<i>t</i> -C ₄ H ₉ OK	<i>t</i> -C ₄ H ₉ OH	 (59)	208,210
NaNH ₂	Et ₂ O	" (62)	873
NaH NaNH ₂ <i>t</i> -C ₄ H ₉ OK KOH	Et ₂ O C ₆ H ₆ <i>t</i> -C ₄ H ₉ OH Aq DMSO	 I,  II	205 205 205 205
NaH	DMF	 (-)	217,874

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₈ (Contd.)	2,5-F ₂ C ₆ H ₃ CH ₂ CN	CH ₃ N[(CH ₂) ₂ Cl] ₂
	2,4-F(Cl)C ₆ H ₃ CH ₂ CN	"
	C ₆ H ₅ CH ₂ CN	C ₂ H ₅ O ₂ CN[(CH ₂) ₂ Br] ₂
		C ₆ H ₅ SO ₂ O(CH ₂) ₂ Cl
		<i>n</i> -C ₄ H ₉ N[(CH ₂) ₂ Cl] ₂
		CH ₂ =C[OP(O)(OCH ₃) ₂]CO ₂ CH ₃
		
		4-CH ₃ C ₆ H ₄ SO ₃ (CH ₂) ₂ Cl
		4-CH ₃ C ₆ H ₄ SO ₃ (CH ₂) ₂ Br
		(<i>E</i>)-C ₆ H ₅ CH=CHSO ₂ CH ₃
		CH ₂ =C(CO ₂ C ₂ H ₅)OP(O)(OC ₂ H ₅) ₂
		C ₆ H ₅ CH ₂ N[(CH ₂) ₂ Cl] ₂

NITRILE-STABILIZED CARBANIONS (Continued)

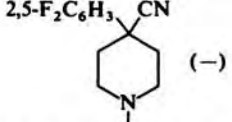
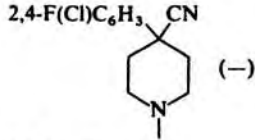
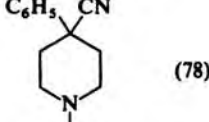
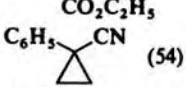
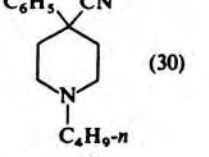
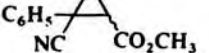
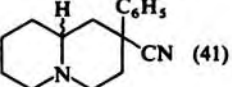
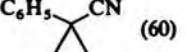
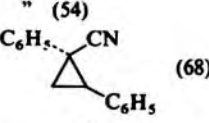
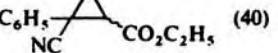
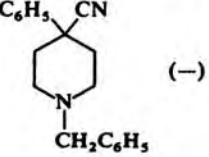
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NaH	DMSO	 (-)	217
"	"	 (-)	217
"	DMF	 (78)	875
NaNH ₂	Et ₂ O	 (54)	184
Aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl		 (30)	214
NaH	DMF	 (247)	247
NaNH ₂	Toluene	 (41)	212
"	Et ₂ O	 (60)	184
"	"	" (54)	184
LDA	THF	 (68)	391
NaH	DMSO	 (40)	246,245
NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	-	 (-)	870

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₈ (Contd.)	4-XC ₆ H ₄ CH ₂ CN	4-CH ₃ C ₆ H ₄ SO ₂ N[(CH ₂) ₂ Cl] ₂
	C ₆ H ₅ CH ₂ CN	(E)-C ₆ H ₅ CH=CHSO ₂ C ₆ H ₅
	4-XC ₆ H ₄ CH ₂ CN	(E)-4-CH ₃ C ₆ H ₄ SO ₃ (CH ₂) ₄ CH=CHCO ₂ CH ₃
	4-XC ₆ H ₄ CH ₂ CN	(4-YC ₆ H ₄ CH=CH) ₂ CO
		4-CH ₃ OC ₆ H ₄ CH=CHCOCH=CHC ₆ H ₅
C ₉	Cl(CH ₂) ₃ CH(C ₄ H ₉ -i)CN	—
	Cl(CH ₂) ₄ CH(C ₃ H ₇ -i)CN	—
		—

NITRILE-STABILIZED CARBANIONS (Continued)

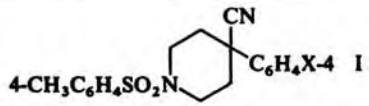
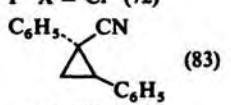
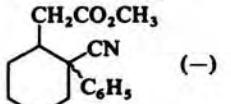
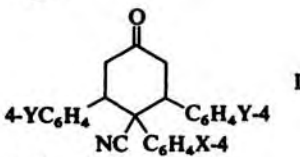
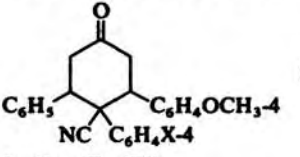
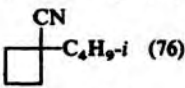
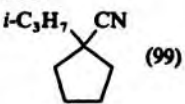
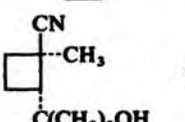
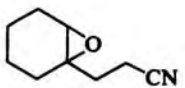
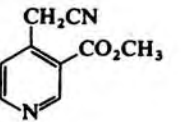
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl		 4-CH ₃ C ₆ H ₄ SO ₂ N(C ₆ H ₄ X-4) I I X = H (68) I X = Cl (72)	876,870 215
LDA	THF	 C ₆ H ₅ -C(CN)-C ₂ H ₄ (83)	391
<i>t</i> -C ₄ H ₉ OK	<i>t</i> -C ₄ H ₉ OH	 C ₆ H ₅ -C(CN)-C ₅ H ₁₀ (-)	229
NaOH	CH ₃ OH	 4-YC ₆ H ₄ -C ₆ H ₄ (CN)-C ₆ H ₄ X-4 I I X = H, Y = H (85) I X = Cl, Y = H (83) I X = NO ₂ , Y = H (85) I X = NO ₂ , Y = CH ₃ (88) I X = Cl, Y = CH ₃ (85) I X = NO ₂ , Y = OCH ₃ (78)	856 856 856 856 856 856
"	"	 C ₆ H ₅ -C ₆ H ₄ (CN)-C ₆ H ₄ OCH ₃ -4 I I X = Cl (86) I X = NO ₂ (80)	856 856
LiN(C ₂ H ₅) ₂	HMPA	 C ₆ H ₅ -C(CN)-C ₃ H ₆ -i (76)	193
"	"	 <i>i</i> -C ₃ H ₇ -C(CN)-C ₄ H ₈ (99)	193
NaN[Si(CH ₃) ₃] ₂	C ₆ H ₆ , 80°	 C ₆ H ₅ -C(CN)-C ₃ H ₆ -i (58) C(CH ₃) ₂ OH	222

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₉ (Contd.)		—
	2-ClC ₆ H ₄ (CH ₂) ₂ CN	—
	4-CH ₃ OC ₆ H ₄ CH ₂ CN	Br(CH ₂) ₂ Br
	3,4-(CH ₂ O ₂)C ₆ H ₃ CH ₂ CN	"
	3-CH ₃ OC ₆ H ₄ CH ₂ CN	Br(CH ₂) ₃ Br
		Br(CH ₂) ₄ Br
		"
	4-CH ₃ C ₆ H ₄ CH ₂ CN	"
	4-CH ₃ OC ₆ H ₄ CH ₂ CN	Cl(CH ₂) ₄ Cl
		Br(CH ₂) ₄ Br
		Br(CH ₂) ₄ Br ^a
	3,4-(CH ₂ O ₂)C ₆ H ₃ CH ₂ CN	"
		(Z)-ClCH ₂ CH=CHCH ₂ Cl

NITRILE-STABILIZED CARBANIONS (Continued)

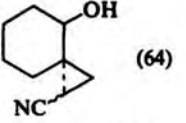
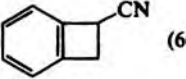
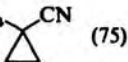
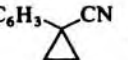
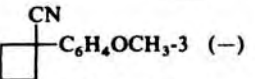
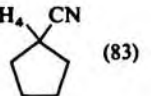
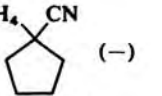
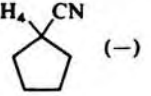
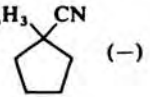
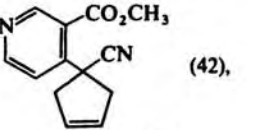
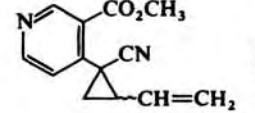
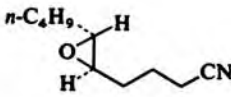
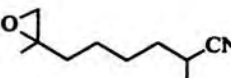
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
KNH ₂	NH ₃	 (64)	221
"	"	 (66)	877,273
NaNH ₂	"	" (65)	274
LiNH ₂	DME	4-CH ₃ OC ₆ H ₄  (75)	189
"	"	3,4-(CH ₂ O ₂)C ₆ H ₃  (65-75)	188
NaNH ₂	—	 (—)	191
NaOH	—	3-CH ₃ OC ₆ H ₄  (83)	199
NaNH ₂	—	"	191
"	—	4-CH ₃ C ₆ H ₄  (—)	191
"	Toluene	4-CH ₃ OC ₆ H ₄  (—)	195
NaOH	—	" (76)	199
KOH, [C ₆ H ₅ CH ₂ N(CH ₃) ₃]OH	HO(CH ₂) ₂ OH	" (89)	201,202
NaNH ₂	—	3,4-(CH ₂ O ₂)C ₆ H ₃  (—)	191
NaH	THF	 (42),	207
		 ("Small amount")	

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₉ (Contd.)	3-CH ₃ OC ₆ H ₄ CH ₂ CN	Br(CH ₂) ₃ Br
	4-CH ₃ C ₆ H ₄ CH ₂ CN	Br(CH ₂) ₃ Br ^a
	3,4-(CH ₂ O ₂)C ₆ H ₃ CH ₂ CN	Br(CH ₂) ₃ Br
	3-CH ₃ OC ₆ H ₄ CH ₂ CN	(E)-ClCH=CHCH ₂ N[(CH ₂) ₂ Cl] ₂
		4-CH ₃ C ₆ H ₄ SO ₂ N[(CH ₂) ₂ Cl] ₂
	3-CH ₃ OC ₆ H ₄ CH ₂ CN	(E)-4-CH ₃ C ₆ H ₃ SO ₂ O(CH ₂) ₄ CH=CHCO ₂ CH ₃
C ₁₀		—
		—

NITRILE-STABILIZED CARBANIONS (Continued)

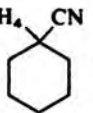
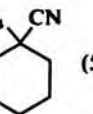
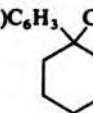
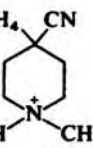
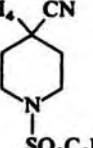
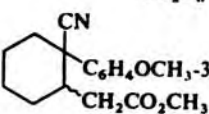
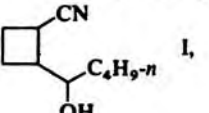
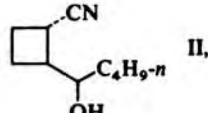
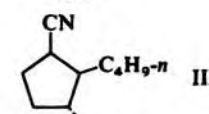
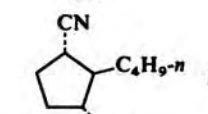
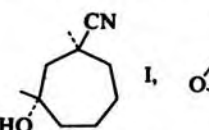
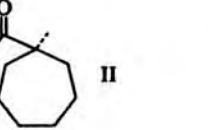
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
NaNH ₂	—	3-CH ₃ OC ₆ H ₄  (—)	191	
40% NaOH. (CH ₃) ₄ Ni	C ₆ H ₆	4-CH ₃ C ₆ H ₄  (53)	201,20	
NaNH ₂	—	3,4-(CH ₂ O ₂)C ₆ H ₃  (—)	191	
"	Toluene	3-CH ₃ OC ₆ H ₄  Cl ⁻ (67)	213	
"	"	3-CH ₃ OC ₆ H ₄  SO ₂ C ₆ H ₄ CH ₃ -4 (—)	878	
<i>t</i> -C ₄ H ₉ OK	<i>t</i> -C ₄ H ₉ OH	 (—)	229	
NaNH ₂	THF, 40°	 I,  II,	I + II:III + IV = 36:64 (88)	224
		 III,  IV		
KNH ₂	NH ₃ , DME	 I,  II	I:II = 1.6:1 (65)	221

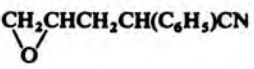
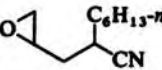
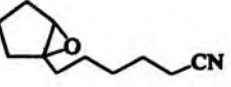
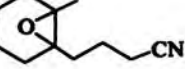
TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₁₀ (Contd.)		—
		—
		—
		—
	2,4-Br(CH ₃ O)C ₆ H ₃ (CH ₂) ₂ CN	
	2-ClC ₆ H ₄ (CH ₂) ₃ CN	
	3-ClC ₆ H ₄ (CH ₂) ₃ CN	
	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN	Cl(CH ₂) ₂ Cl
		Br(CH ₂) ₂ Br
	2,6-(CH ₃ O) ₂ C ₆ H ₃ SCH ₂ CN	Cl(CH ₂) ₂ Cl
	2,4-(CH ₃) ₂ C ₆ H ₃ CH ₂ CN	Br(CH ₂) ₄ Br
	2,5-(CH ₃) ₂ C ₆ H ₃ CH ₂ CN	"

NITRILE-STABILIZED CARBANIONS (Continued)

Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
KNH ₂	NH ₃ , DME	(80)	221
"	"	I, II,	
		III, IV	
NaNH ₂	THF, 40°	I + II:III + IV = 35:65 (88)	224
KNH ₂	NH ₃ , DME	(75)	223
<i>t</i> -C ₄ H ₉ OK	DMSO, 45°	(-)	219
NaNH ₂	NH ₃	(55)	877,275
KNH ₂	"	(68)	273
"	"	" (49)	273
LDA	HMPA, THF	3,4-(CH ₃ O) ₂ C ₆ H ₃ (86)	107
<i>n</i> -C ₄ H ₉ Li	THF, -76°	" (24)	102
LDA	THF, HMPA, -78°	2,6-(CH ₃ O) ₂ C ₆ H ₃ S (90)	879
NaNH ₂	—	2,4-(CH ₃) ₂ C ₆ H ₃ (-)	191
"	—	2,5-(CH ₃) ₂ C ₆ H ₃ (-)	191

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₁₀ (Contd.)	3,4-(CH ₃) ₂ C ₆ H ₃ CH ₂ CN	Br(CH ₂) ₄ Cl
	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN	"
		Br(CH ₂) ₃ Br
	2-(CH ₃ OCH ₂ O)C ₆ H ₄ CH ₂ CN	C ₆ H ₅ CH ₂ N[(CH ₂) ₂ Cl] ₂
C ₁₁	<i>i</i> -C ₄ H ₉ CH(OSO ₂ CH ₃)C(CH ₃) ₂ CH ₂ CN	—
		—
	—	—
		—
	—	—
		—
	—	

NITRILE-STABILIZED CARBANIONS (Continued)



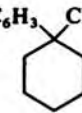
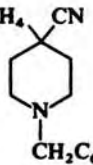
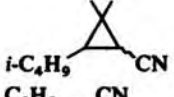
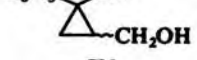
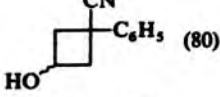
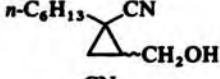
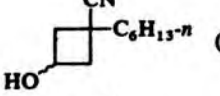
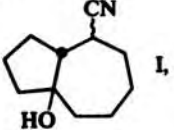
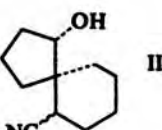
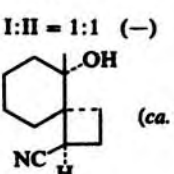
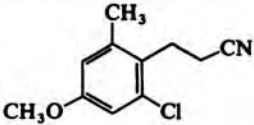
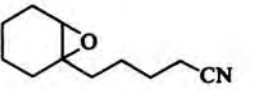
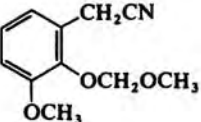
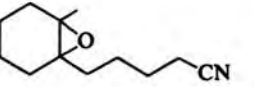
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
"	—	3,4-(CH ₃) ₂ C ₆ H ₃  (—)	191
"	—	3,4-(CH ₃ O) ₂ C ₆ H ₃  (—)	191
NaH	Toluene	3,4-(CH ₃ O) ₂ C ₆ H ₃  (—)	880
"	DMSO	2-CH ₃ OCH ₂ OC ₆ H ₄  (80–90)	688
"	DMF, 20°	 (86, <i>E:Z</i> = 40:60)	559
LDA	—	 (94)	220
CH ₃ MgI, MgBr ₂	—	 (80)	220
LDA	—	 (43)	220
CH ₃ MgI (2 eq)	—	 (40)	220
KNH ₂	NH ₃ , DME	 I,  II I:II = 1:1 (—)	221
"	"	 (ca. 80)	222

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₁₁ (Contd.)		—
	<i>n</i> -C ₆ H ₁₃ CH[(CH ₂) ₃ Cl]CN	—
		—
	2-ClC ₆ H ₄ (CH ₂) ₄ CN	—
	Cl(CH ₂) ₆ CH(C ₃ H ₇ - <i>i</i>)CN	—
		C ₆ H ₅ CH ₂ N[(CH ₂) ₂ Cl] ₂
C ₁₂	2-ClC ₆ H ₄ (CH ₂) ₅ CN	—
		—
	1-Naphthylacetonitrile	Br(CH ₂) ₂ Br
	Cyanomethylferrocene	Cl(CH ₂) ₂ Cl
	1-Naphthylacetonitrile	Br(CH ₂) ₃ Br
		Br(CH ₂) ₄ Br

NITRILE-STABILIZED CARBANIONS (Continued)

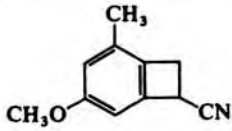

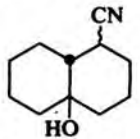
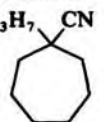
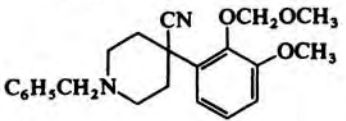
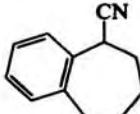
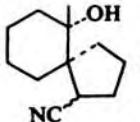


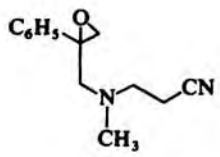
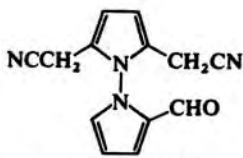
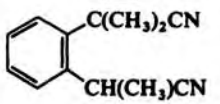
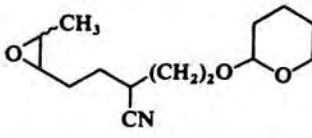
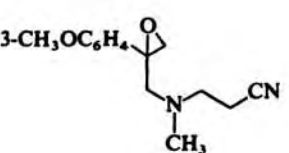
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NaNH ₂	NH ₃	 (—)	275
LiN(C ₂ H ₅) ₂	HMPA	 -C ₆ H ₁₃ - <i>n</i> (56)	193
KNH ₂	NH ₃ , DME	 (ca. 70)	223
"	NH ₃	1-Cyanotetralin (61)	273
LiN(C ₂ H ₅) ₂	HMPA	 (46)	193
NaH	DMSO	 (65-75)	688
KNH ₂	NH ₃	 (49)	273
"	NH ₃ , DME	 (80)	221
50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	—	1-C ₁₀ H ₇ -1 (67)	97
<i>n</i> -C ₄ H ₉ Li	Et ₂ O	 (53)	49
50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	—	 -C ₁₀ H ₇ -1 (21)	97
"	—	1-C ₁₀ H ₇ -1 (80)	97

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₁₂ (Contd.)	1-Naphthylacetonitrile	Br(CH ₂) ₃ Br
C ₁₃		—
		—
		CH ₃ I
C ₁₄		—
		—

NITRILE-STABILIZED CARBANIONS (Continued)

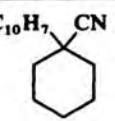
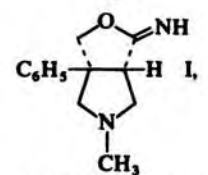
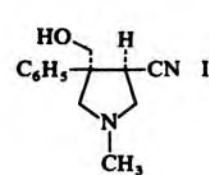
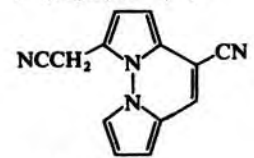
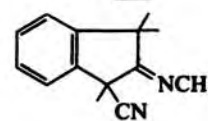
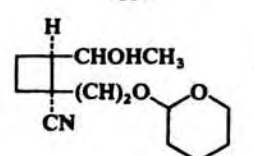
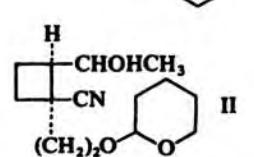
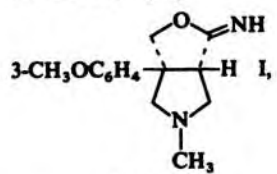
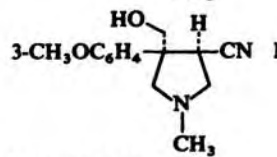
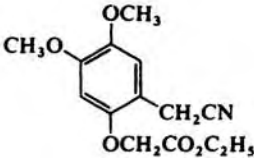
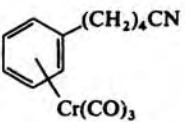
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	—	1-C ₁₀ H ₇  (17)	97
KNH ₂	NH ₃ , Et ₂ O	 I,  II	225
		I (major), II (—)	
Piperidine	Py	 (80)	881
CH ₃ Li	Et ₂ O, THF	 (90)	45
LiN[Si(CH ₃) ₃] ₂	C ₆ H ₆ , 0°	 I,  II	222
		I:II = 95:5 (—)	
KNH ₂	NH ₃ , Et ₂ O	 I,  II	225
		I (major), II (—)	

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₁₄ (Contd.)	4-CH ₃ C ₆ H ₄ SO ₃ CH ₂ C(CH ₃) ₂ (CH ₂) ₂ CN	—
		—
		—
	4-C ₆ H ₅ C ₆ H ₄ CH ₂ CN	Br(CH ₂) ₂ Br
		Br(CH ₂) ₃ Br
		Br(CH ₂) ₄ Br
	(C ₆ H ₅) ₂ CHCN	Cl(CH ₂) ₃ CN
	2-(4-ClC ₆ H ₄ O)C ₆ H ₄ CH ₂ CN	CH ₃ N[(CH ₂) ₂ Cl] ₂
	2-(4-ClC ₆ H ₄ S)C ₆ H ₄ CH ₂ CN	"

NITRILE-STABILIZED CARBANIONS (Continued)

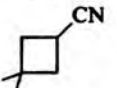
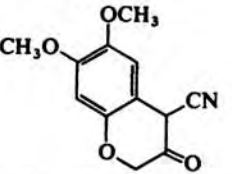
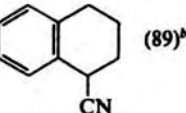
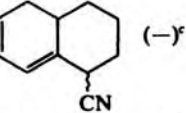

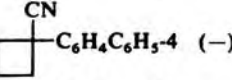

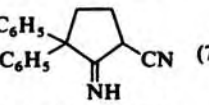
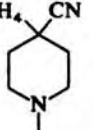

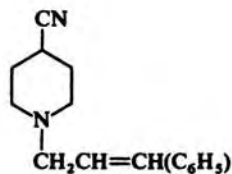
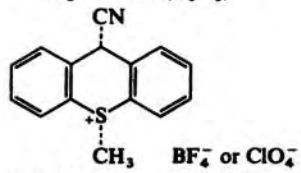
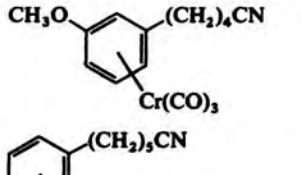
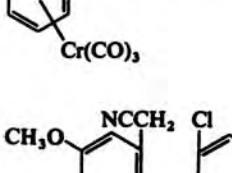
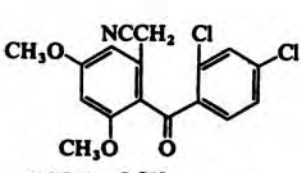
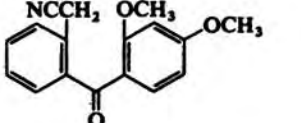
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NaNH ₂	NH ₃	 (11)	882
"	C ₆ H ₆	" (25)	882
<i>t</i> -C ₃ H ₁₁ ONa	"	" (43)	882
Na	Toluene	 (71)	883
LDA	THF	 (89) ^b	146
"	"	 (-) ^c	146,285
NaNH ₂	Et ₂ O	4-C ₆ H ₅ C ₆ H ₄  (-)	192
"	"	 (-)	192
"	"	4-C ₆ H ₅ C ₆ H ₄  (-)	192
"	NH ₃ , Et ₂ O	 (70)	228
NaH	DMSO	2-(4-ClC ₆ H ₄ O)C ₆ H ₄  (-)	884
"	"	2-(4-ClC ₆ H ₄ S)C ₆ H ₄  (-)	885

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₁₄ (Contd.)	2-(4-XC ₆ H ₄ O)C ₆ H ₄ CH ₂ CN	CH ₃ N[(CH ₂) ₂ Cl] ₂
	(C ₆ H ₅) ₂ CHCN	Cl(CH ₂) ₄ CN
C ₁₅	   	—
C ₁₇	 	—

NITRILE-STABILIZED CARBANIONS (Continued)

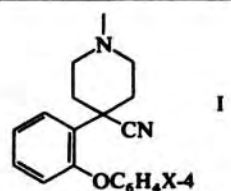
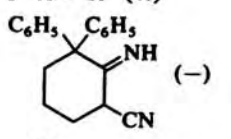
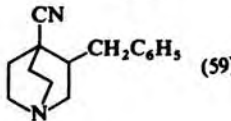
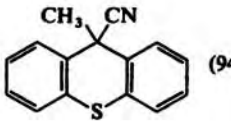
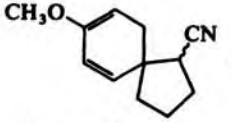
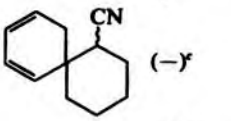
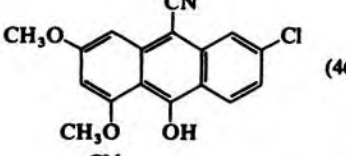
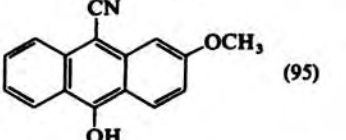
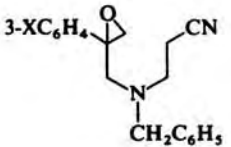
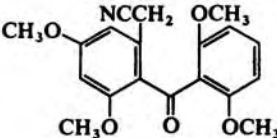
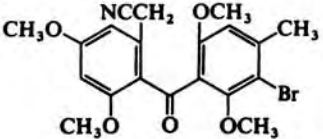
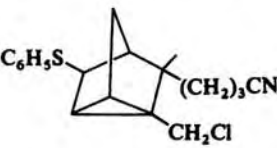
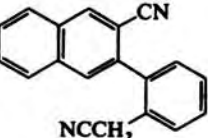
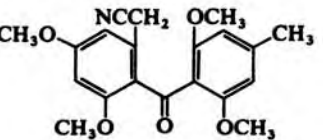
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NaH	DMF	 I I X = H (90) I X = F (81) I X = Cl (46)	216 216 216
NaNH ₂	"	 (-)	769
LiN(C ₂ H ₅) ₂	THF	 (59)	398
NaH	"	 (94)	52
LDA	"	 (70) ^d	285
"	"	 (-) ^f	146
<i>t</i> -C ₄ H ₉ OK	DMF	 (46)	271
NaOCH ₃	DMSO	 (95)	155

TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₁₉ -C ₂₀		—
		—
		—
	C ₆ H ₅ CH(CN)(CH ₂) ₂ CH ₂ N(CH ₃)CH ₂ C ₆ H ₅	Br(CH ₂) ₂ Cl
		—
		—
C ₂₀		—

NITRILE-STABILIZED CARBANIONS (Continued)

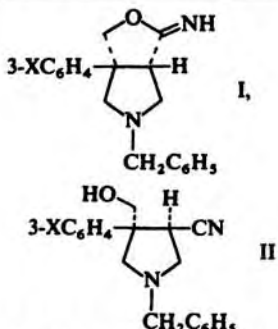
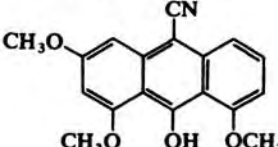
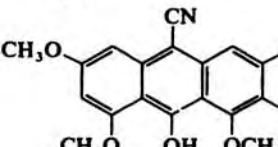
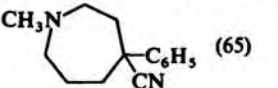
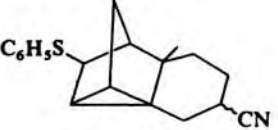
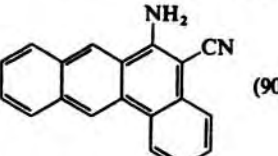
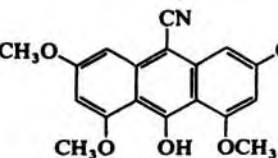
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
			
KNH ₂	NH ₃ , Et ₂ O	X = H, I (major isomer), II (—)	225
"	"	X = OCH ₃ , "	225
NaOCH ₃	DMSO	 (94)	269,886
"	DMF	" (80)	269,886
"	DMSO	 (—)	270
Na	NH ₃ , toluene	 (65)	887
LiN(C ₂ H ₅) ₂	THF, HMPA, -78°	 (81)	888
<i>i</i> -C ₄ H ₉ OK	—	 (90)	865
NaOCH ₃	DMSO	 (—)	269

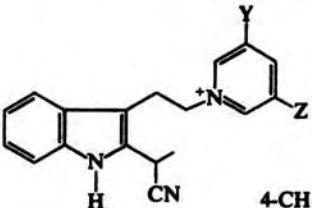
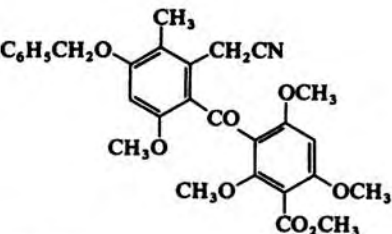
TABLE VII. INTRAMOLECULAR REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile
C ₂₁		—
	(C ₆ H ₅) ₂ CHCH(C ₆ H ₅)CN	CH ₂ Cl ₂
C ₂₃		—
		—
		—
C ₂₅		—
		—
	4-CH ₃ C ₆ H ₄ SO ₃ ⁻	—

NITRILE-STABILIZED CARBANIONS (Continued)

Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
NaOCH ₃	DMF		269
KNH ₂	NH ₃ , Et ₂ O		109
NaOCH ₃	DMSO		268
		I:II = 1:1 (—)	
NaH	THF		889
NaHCO ₃	CH ₂ Cl ₂	I Y = H, Z = CN (90)	890
"	CHCl ₃	I Y = Z = CO ₂ CH ₃ (80)	890
"	CH ₃ OH	I Y = Z = CO ₂ CH ₃ (89)	890

TABLE VII. INTRAMOLECULAR REACTIONS OF

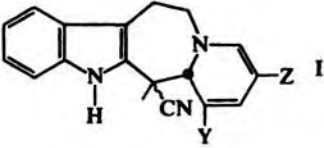
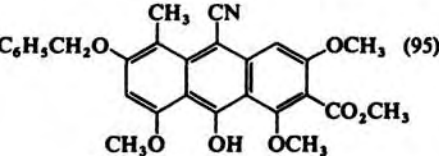
No. of C Atoms	Nucleophile	Electrophile
C ₂₆ -C ₂₉		—
	4-CH ₃ C ₆ H ₄ SO ₃ ⁻	
C ₂₉		—

^a The precise leaving group in the alkylating agent was unspecified.

^b The initial product was oxidized with iodine.

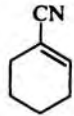
^c The initial product was quenched with CF₃CO₂H at low temperature and oxidized with iodine.

NITRILE-STABILIZED CARBANIONS (*Continued*)

Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₃ N	CH ₂ Cl ₂	 I	
		I Y = H, Z = CN <i>cis:trans</i> = 32:68 (50)	891
		I Y = H, Z = CO ₂ CH ₃ <i>trans</i> (98)	891
		I Y = Z = CO ₂ CH ₃ <i>cis:trans</i> = 8:92 (79)	891
<i>t</i> -C ₄ H ₉ OK	DMF	 (95)	271

^d The initial product was quenched with CF₃CO₂H at low temperature and exposed to aqueous ammonium hydroxide.

TABLE VIII. ALKYLATION OF UNSATURATED

No. of C Atoms	Nucleophile	Electrophile	Base	
C ₄	CH ₂ =CHCH ₂ CN	CH ₃ I	CH ₃ Li	
		"	LDA	
		<i>i</i> -C ₃ H ₇ I	"	
		CH ₂ =CHCH ₂ Br	"	
		HC≡CCH ₂ Br	"	
		CH ₃ C(Cl)=CHCH ₂ Br	"	
		<i>n</i> -C ₄ H ₉ I	"	
		BrCH ₂ CO ₂ C ₂ H ₅	"	
		C ₆ H ₅ CH ₂ Br	"	
		"	CH ₃ Li	
C ₅	CH ₃ CH=CHCN	<i>n</i> -C ₈ H ₁₇ Br	LDA	
	(CH ₃) ₂ C=CHCN or CH ₂ =C(CH ₃)CH ₂ CN	CH ₃ I	NaNH ₂	
	CH ₃ CH=CHCH ₂ CN	<i>n</i> -C ₃ H ₇ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	
	(CH ₃) ₂ C=CHCN	(CH ₃) ₂ C=CHCH ₂ Cl	KOH	
C ₆	<i>i</i> -C ₃ H ₇ CH=CHCN (CH ₃) ₂ C=CHCH ₂ CN (<i>E/Z</i>)-C ₂ H ₅ (CH ₃)C=CHCN (CH ₃) ₂ C=C(CH ₃)CN NCCH ₂ CH=CHCH ₂ CN	CH ₃ I	NaNH ₂	
		"	"	
		"	"	
		"	"	
		"	NaOH	
		C ₂ H ₅ I ^a <i>n</i> -C ₄ H ₉ I ^a	"	
C ₇	CH ₂ =CHCH(CH ₂ CH=CH ₂)CN	CH ₃ I	LDA	
		<i>i</i> -C ₃ H ₇ I	"	
		CH ₂ =CHCH ₂ Br	"	
		<i>n</i> -C ₄ H ₉ Br	"	
		CH ₃ C(Cl)=CHCH ₂ Br	"	
		BrCH ₂ CO ₂ C ₂ H ₅	"	
		(CH ₃) ₂ C=C(CH ₃)CH ₂ CN	CH ₃ I	NaNH ₂
		"	"	
		CH ₂ =CHCH(CH ₂ CO ₂ CH ₃)CN	"	LiN[Si(CH ₃) ₃] ₂
		CH ₂ =CHCH ₂ Br	"	"
	<i>n</i> -C ₄ H ₉ I	"	"	
	CH ₃ C(Cl)=CHCH ₂ Br	"	"	
	BrCH ₂ CO ₂ C ₂ H ₅	"	"	
C ₇		CH ₃ I	LDA	
		"	LDA, tetramethyl-12-crown-4	
		<i>i</i> -C ₃ H ₇ I ^a	LDA	

NITRILES WITH ALKYL HALIDES

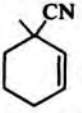
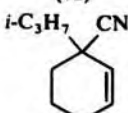
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Ether, THF, -100°	CH ₂ =CHC(CH ₃) ₂ CN (64)	44
THF, -78°	CH ₂ =CHCH(CH ₃)CN (75)	399
"	CH ₂ =CHCH(C ₃ H _{7-<i>i</i>)CN (72)}	399
"	CH ₂ =CHCH(CH ₂ CH=CH ₂)CN (98)	399
"	CH ₂ =CHCH(CH ₂ C≡CH)CN (90)	399
"	CH ₂ =CHCH[CH ₂ CH=C(Cl)CH ₃]CN (97)	399
"	CH ₂ =CHCH(C ₄ H _{9-<i>n</i>)CN (90)}	399
"	CH ₂ =CHCH(CH ₂ CO ₂ C ₂ H ₅)CN (95)	399
"	CH ₂ =CHCH(CH ₂ C ₆ H ₅)CN (95)	399
Et ₂ O, THF, -100°	CH ₂ =CHC(CH ₂ C ₆ H ₅) ₂ CN (70-80)	103
THF, HMPA, -78°	CH ₂ =CHC(C ₈ H _{17-<i>n</i>)₂CN (-)}	165
NH ₃	CH ₂ =C(CH ₃)C(CH ₃) ₂ CN (40)	403
	CH ₃ CH=CHCH(C ₃ H _{7-<i>n</i>)CN (74)}	570
DMSO	(CH ₃) ₂ C=C(CN)CH ₂ CH=C(CH ₃) ₂ (55) (<i>E</i>) and (<i>Z</i>)-(CH ₃) ₂ C=CH(CH ₂) ₂ C(CH ₃)=CHCN (7)	400
NH ₃	(CH ₃) ₂ C=CHC(CH ₃) ₂ CN (traces)	403
"	" (34)	403
"	(<i>E</i>)- and (<i>Z</i>)-CH ₃ CH=C(CH ₃)C(CH ₃) ₂ CN (31)	403
"	CH ₂ =C(CH ₃)C(CH ₃) ₂ CN (83)	403
DMF	NCC(CH ₃) ₂ CH=CHC(CH ₃) ₂ CN (72)	404
"	NCC(C ₂ H ₅) ₂ CH=CHC(C ₂ H ₅) ₂ CN (-)	404
"	NCC(C ₄ H _{9-<i>n</i>)₂CH=CHC(C₄H_{9-<i>n</i>)₂CN (-)}}	404
THF, -78°	CH ₂ =CHC(CH ₂ CH=CH ₂)(CH ₃)CN (86)	399
"	CH ₂ =CHCH ₂ C(CH=CH ₂)(C ₃ H _{7-<i>i</i>)CN (95)}	399
"	CH ₂ =CHC(CH ₂ CH=CH ₂) ₂ CN (94)	399
"	CH ₂ =CHC(CH ₂ CH=CH ₂)(C ₄ H _{9-<i>n</i>)CN (83)}	399
"	CH ₂ =CHC(CH ₂ CH=CH ₂)[CH ₂ CH=C(Cl)CH ₃]CN (97)	399
"	CH ₂ =CHC(CH ₂ CH=CH ₂)(CH ₂ CO ₂ C ₂ H ₅)CN (95)	399
NH ₃	CH ₂ =C(C ₃ H _{7-<i>i</i>)C(CH₃)₂CN (38)}	403
"	(CH ₃) ₂ C=C(CH ₃)C(CH ₃) ₂ CN (44)	402
THF, -78°	CH ₂ =CHC(CH ₂ CO ₂ C ₂ H ₅)(CH ₃)CN (86)	399
"	CH ₂ =CHC(CH ₂ CH=CH ₂)(CH ₂ CO ₂ CH ₃)CN (98)	399
"	CH ₂ =CHC(C ₄ H _{9-<i>n</i>)CH₂CO₂CH₃)CN (90)}	399
"	CH ₂ =CHC(CH ₂ CO ₂ CH ₃)[CH ₂ CH=C(Cl)CH ₃]CN (92)	399
"	CH ₂ =CHC(CH ₂ CO ₂ CH ₃)(CH ₂ CO ₂ C ₂ H ₅)CN (97)	399
HMPA, THF	 (78)	401
THF	" (72)	401
HMPA, THF	 (63)	401

TABLE VIII. ALKYLATION OF UNSATURATED

No. of C Atoms	Nucleophile	Electrophile	Base
C ₇ (Contd.)		(CH ₃) ₂ C=CHCH ₂ Br ^a	LDA
	CH ₂ =CHCH(CH ₂ CH=CH ₂)CN	C ₆ H ₅ CH ₂ Br	"
	CH ₂ =CHCH(CH ₂ CO ₂ CH ₃)CN	"	LiN[Si(CH ₃) ₃] ₂
C ₈		CH ₃ I	LDA
	2-CH ₃ C ₆ H ₄ CN	<i>i</i> -C ₃ H ₇ Br ^a	KNH ₂
		Br(CH ₂) ₄ Br	NaNH ₂
		(CH ₃) ₂ CBrC(CH ₃) ₂ Br	"
		<i>n</i> -C ₅ H ₁₁ Br ^a	KNH ₂
		C ₆ H ₅ CH ₂ Cl	NaNH ₂
		"	KNH ₂
		4-ClC ₆ H ₄ CH ₂ Cl	NaNH ₂
		4-CH ₃ C ₆ H ₄ CH ₂ Cl ^a	"
	3-CH ₃ C ₆ H ₄ CN	<i>n</i> -C ₃ H ₇ Br	LDA
	<i>n</i> -C ₅ H ₁₁ Br ^a	"	
	<i>n</i> -C ₆ H ₁₃ Br	"	
4-CH ₃ C ₆ H ₄ CN	<i>n</i> -C ₄ H ₉ Br	NaNH ₂	
	Br(CH ₂) ₄ Br	"	
	(CH ₃) ₂ CBrC(CH ₃) ₂ Br	"	
	C ₆ H ₅ CH ₂ Cl	"	
	"	LDA	
	4-ClC ₆ H ₄ CH ₂ Cl	NaNH ₂	
C ₁₀		CH ₃ I	LDA
		C ₆ H ₅ CH ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(CH ₃) ₃]Cl
			LICA
C ₁₁		X(CH ₂) ₂ Cl	NaNH ₂
			"
C ₁₃		CH ₃ I	LDA

NITRILES WITH ALKYL HALIDES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
HMPA, THF	(55)	401
THF, -78°	CH ₂ =CHC(CH ₂ CH=CH ₂)(CH ₂ C ₆ H ₅)CN (97)	399
"	CH ₂ =CHC(CH ₂ C ₆ H ₅)(CH ₂ CO ₂ CH ₃)CN (97)	399
THF, HMPA	(-)	206
NH ₃ , Et ₂ O	2- <i>i</i> -C ₄ H ₉ C ₆ H ₄ CN (69)	405
"	[2-NCC ₆ H ₄ (CH ₂) ₃] ₂ (67)	407
"	(2-NCC ₆ H ₄ CH ₂) ₂ (52)	407
"	2- <i>n</i> -C ₆ H ₁₃ C ₆ H ₄ CN (66)	405
"	2-NCC ₆ H ₄ (CH ₂) ₂ C ₆ H ₅ (77)	406,407
"	" (81)	405
"	2-NCC ₆ H ₄ (CH ₂) ₂ C ₆ H ₄ Cl-4 (64)	407
NH ₃	2-NCC ₆ H ₄ (CH ₂) ₂ C ₆ H ₄ CH ₃ -4 (21)	405
THF, HMPA, -78°	3- <i>n</i> -C ₄ H ₉ C ₆ H ₄ CN (37)	408
"	3- <i>n</i> -C ₆ H ₁₃ C ₆ H ₄ CN (30)	408
"	3- <i>n</i> -C ₇ H ₁₅ C ₆ H ₄ CN (34)	408
NH ₃ , Et ₂ O	4- <i>n</i> -C ₅ H ₁₁ C ₆ H ₄ CN (63)	407
"	[4-NCC ₆ H ₄ (CH ₂) ₃] ₂ (63)	406,407
"	(4-NCC ₆ H ₄ CH ₂) ₂ (55)	407
"	4-NCC ₆ H ₄ (CH ₂) ₂ C ₆ H ₅ (71)	406,407
"	" (75)	408
THF, HMPA, -78°	4-NCC ₆ H ₄ (CH ₂) ₂ C ₆ H ₄ Cl-4 (86)	407
NH ₃ , Et ₂ O		
THF, HMPA	(98)	206
90-100°	(-)	892
THF, HMPA, -25°	(80)	893
Toluene	I	I X = N(CH ₃) ₂ (-)
"		I X = N(CH ₂) ₅ (-)
THF, HMPA	(98)	206

TABLE VIII. ALKYLATION OF UNSATURATED

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₃ (Contd.)		X(CH ₂) ₂ Cl	
			NaNH ₂ "
C ₁₄		(CH ₃) ₂ N(CH ₂) ₂ Cl	"
		n-C ₃ H ₇ Br	C ₁₀ H ₈ Na
C ₁₅		X(CH ₂) ₂ Cl	NaNH ₂ " " " "
		X(CH ₂) ₂ Cl	"
		X(CH ₂) ₂ Cl	"
		X(CH ₂) ₂ Cl	"
		X(CH ₂) ₂ Cl	"
C ₁ -18		2-[C ₆ H ₅ (CH ₂) ₂]C ₆ H ₄ CN 4-[C ₆ H ₅ (CH ₂) ₂]C ₆ H ₄ CN	C ₆ H ₅ CH ₂ Cl Br(CH ₂) ₄ Br
		CH ₃ I n-C ₃ H ₇ Br ^a i-C ₃ H ₇ Br ^a CH ₃ I	" " " "
		CH ₃ I C ₂ H ₅ Br ^a CH ₃ I	" " "

^a The precise leaving group in the alkylating agent was unspecified.

NITRILES WITH ALKYL HALIDES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Toluene	 I X = N(CH ₃) ₂ (-)	339
"	I X = N(CH ₂) ₅ (-)	339
"	 (-)	339
THF	 (-)	198
Toluene	 I X = N(CH ₃) ₂ (69)	339
"	I X = N(C ₂ H ₅) ₂ (-)	339
"	I X = N(CH ₂) ₄ (-)	339
"	I X = N(CH ₂) ₅ (-)	339
"	I X = CH ₂ N(CH ₂) ₅ (-)	339
NH ₃ , Et ₂ O	 I X = N(CH ₃) ₂ (-)	339
"	I X = N(CH ₂) ₅ (-)	339
"	2-[(C ₆ H ₅ CH ₂) ₂ CH]C ₆ H ₄ CN (44)	407
"	(4-NCC ₆ H ₄ CH(CH ₂ C ₆ H ₅)CH ₂ CH ₂) ₂ (20)	407
NH ₃	 I R = CH ₃ , X = H (95)	894
"	I R = C ₃ H _{7-n} , X = H (92)	894
"	I R = C ₃ H _{7-i} , X = H (91)	894
"	I R = CH ₃ , X = OCH ₃ (80)	894
"	 II R = CH ₃ , X = H (72)	894
"	II R = C ₂ H ₅ , X = H (72)	894
"	II R = CH ₃ , X = OCH ₃ (91)	894

TABLE IX. ACYLATION OF UNSATURATED NITRILE-STABILIZED CARBANIONS WITH CARBOXYLIC ESTERS AND NITRILES

No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₈	2-CH ₃ C ₆ H ₄ CN	C ₂ H ₅ CO ₂ CH ₃ ^a	KNH ₂	NH ₃ , Et ₂ O	2-NCC ₆ H ₄ CH ₂ COC ₂ H ₅ (42)	405	
		<i>i</i> -C ₃ H ₇ CO ₂ CH ₃ ^a	"	"	2-NCC ₆ H ₄ CH ₂ COC ₃ H _{7-<i>i</i>} (51)	405	
		C ₆ H ₅ CO ₂ CH ₃	"	"	2-NCC ₆ H ₄ CH ₂ COC ₆ H ₅ (66)	405	
	4-CH ₃ C ₆ H ₄ CN	"	"	NaNH ₂	NH ₃	" (40)	406
		4-CH ₃ C ₆ H ₄ CO ₂ CH ₃	4-CH ₃ C ₆ H ₄ CO ₂ CH ₃	"	"	2-NCC ₆ H ₄ CH ₂ COC ₆ H ₄ CH ₃₋₄ (46)	405
		4-CH ₃ C ₆ H ₄ CN	4-CH ₃ C ₆ H ₄ CN	LDA	THF, HMPA, -78°	4-NCC ₆ H ₄ CH ₂ COC ₆ H ₄ CH ₃₋₄ (76) ^b	408

^a The precise leaving group in the electrophile was unspecified.

^b The initial product was hydrolyzed.

TABLE X. ADDITION OF UNSATURATED NITRILE-STABILIZED CARBANIONS TO ALDEHYDES, KETONES, AND VARIOUS MICHAEL ACCEPTORS

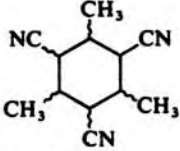
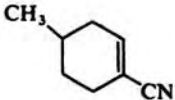
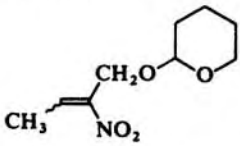
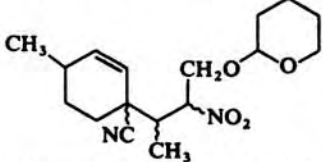
No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄	CH ₃ CH=CHCN	CH ₃ CH=CHCN	C ₆ H ₅ CH ₂ K	C ₆ H ₅ CH ₃	CH ₃ CH=C(CN)CH(CH ₃)CH ₂ CN I (20-23),  (67-75)	895
C ₈	4-CH ₃ C ₆ H ₄ CN	4-ClC ₆ H ₄ CHO	[(C ₂ H ₅) ₄ N]CN	CH ₃ CN	I (54)	896
			"	CH ₃ CN, <i>t</i> -C ₄ H ₉ OH	I (52)	896
	4-CH ₃ C ₆ H ₄ CN	4-ClC ₆ H ₄ CHO	LDA	THF, HMPA, -78°	4-NCC ₆ H ₄ CH ₂ CH(OH)C ₆ H ₄ Cl-4 (76)	408
			LTMP	THF, -78°	 (43)	897
	4-CH ₃ C ₆ H ₄ CN	(2-C ₃ H ₄ N)COC ₆ H ₅	LDA	THF, HMPA, -78°	4-NCC ₆ H ₄ CH ₂ COH(C ₃ H ₄ N-2)C ₆ H ₅ (73)	408
	2-CH ₃ C ₆ H ₄ CN	(C ₆ H ₅) ₂ CO	LiN(CH ₃) ₂	"	2-NCC ₆ H ₄ CH ₂ C(C ₆ H ₅) ₂ OH (53)	408
		"	LDA	"	" (40)	408

TABLE X. ADDITION OF UNSATURATED NITRILE-STABILIZED CARBANIONS TO ALDEHYDES, KETONES, AND VARIOUS MICHAEL ACCEPTORS (Continued)

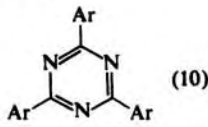
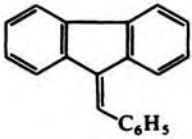
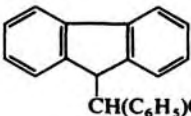
No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ (Contd.)	3-CH ₃ C ₆ H ₄ CN	(C ₆ H ₅) ₂ CO	LiN(CH ₃) ₂	THF, HMPA, -78°	 (10), Ar = 3-CH ₃ C ₆ H ₄	408
	4-CH ₃ C ₆ H ₄ CN	"	LDA	"	3-CH ₃ C ₆ H ₄ (C=NH)N(CH ₃) ₂ (40)	408
		"	LiN(CH ₃) ₂	"	3-NCC ₆ H ₄ CH ₂ C(C ₆ H ₅) ₂ OH (28-41)	408
		"	LDA	"	4-NCC ₆ H ₄ CH ₂ C(C ₆ H ₅) ₂ OH (67)	408
		"	NaNH ₂	"	" (88)	408
		"	"	"	" (54)	406
	3-CH ₃ C ₆ H ₄ CN	1-C ₁₀ H ₇ COC ₆ H ₅ [4-(CH ₃) ₂ NC ₆ H ₄] ₂ CO	LDA	"	3-NCC ₆ H ₄ CH ₂ C(C ₆ H ₅)(C ₁₀ H ₇ -1)OH (39)	408
			"	"	3-NCC ₆ H ₄ CH ₂ C[C ₆ H ₄ N(CH ₃) ₂ -4] ₂ OH (45)	408
	4-CH ₃ C ₆ H ₄ CN		LiNH ₂	NH ₃ , Et ₂ O	 (77) CH(C ₆ H ₅)CH ₂ C ₆ H ₄ CN-4	396

TABLE XI. INTRAMOLECULAR REACTIONS OF UNSATURATED NITRILE-STABILIZED CARBANIONS

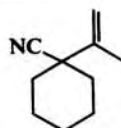
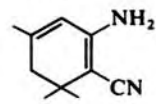
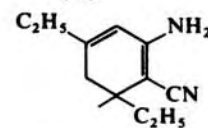
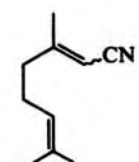
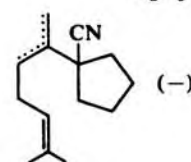
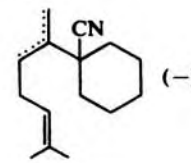
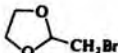
No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅	(CH ₃) ₂ C=CHCN	Br(CH ₂) ₅ Br	LDA	THF, HMPA	 (82)	206
		(CH ₃) ₂ C=CHCN	"	DME	 (90)	898
	CH ₂ =C(CH ₃)CH ₂ CN	CH ₂ =C(CH ₃)CH ₂ CN (CH ₃) ₂ C=CHCN	LiN(C ₂ H ₅) ₂ C ₁₀ H ₈ Li, (C ₂ H ₅) ₂ NH	THF, -78° THF	" (75) " (85)	899 900
C ₆	(C ₂ H ₅)(CH ₃)C=CHCN (E:Z = 60:40)	(C ₂ H ₅)(CH ₃)C=CHCN (E:Z = 60:40)	LDA	DME	 (60)	898
C ₁₀		Br(CH ₂) ₄ Br	"	THF, HMPA	 (-)	206
		Br(CH ₂) ₅ Br	"	"	 (-)	206

TABLE XII. ALKYLATION OF ANIONS OF PROTECTED

No. of C Atoms	Nucleophile	Electrophile	Base
C ₄	(CH ₃ O) ₂ CHCN	<i>n</i> -C ₈ H ₁₇ Br	LDA
C ₇	CH ₂ =CHCH(CN)OSi(CH ₃) ₃	CH ₃ I <i>i</i> -C ₃ H ₇ I CH ₂ =CHCH ₂ Br ^a CH ₃ OCH ₂ Cl <i>i</i> -C ₃ H ₇ Br CH ₂ =CHCH ₂ Br <i>n</i> -C ₈ H ₁₇ Br	" " " " " "
	CH ₂ CH(CN)OCH(OC ₂ H ₅)CH ₃	CH ₃ OCH ₂ Cl <i>i</i> -C ₃ H ₇ Br CH ₂ =CHCH ₂ Br <i>n</i> -C ₈ H ₁₇ Br	" " " "
	CH ₂ =CHCH(CN)OSi(CH ₃) ₂	(CH ₃) ₂ C=CHCH ₂ Br ^a	"
	CH ₂ CH(CN)OCH(OC ₂ H ₅)CH ₃	C ₂ H ₅ Br <i>n</i> -C ₈ H ₁₇ Br C ₆ H ₁₁ Br (<i>Z</i>)-C ₂ H ₅ CH=CH(CH ₂) ₂ I (C ₂ H ₅ O) ₂ CHCH ₂ Br C ₆ H ₅ (CH ₂) ₂ Br <i>n</i> -C ₁₀ H ₂₁ Br	" " " " " " "
C ₈	CH ₂ CH=CHCH(CN)OSi(CH ₃) ₃	CH ₃ I C ₂ H ₅ I Br(CH ₂) ₂ Br <i>i</i> -C ₃ H ₇ Br CH ₂ =CHCH ₂ Br Br(CH ₂) ₂ Br	" " " " " "
	CH ₂ =C(CH ₃)CH(CN)OSi(CH ₃) ₃	CH ₃ I <i>i</i> -C ₃ H ₇ I	" "
	CH ₂ =C(OCH ₃)CH(CN)OSi(CH ₃) ₃	CH ₃ I <i>i</i> -C ₃ H ₇ I C ₆ H ₅ CH ₂ Br	" " "
	CH ₂ =CHCH(CN)OCH(OC ₂ H ₅)CH ₃	(<i>E</i>)-ClCH=CHCH ₂ Cl (<i>Z</i>)-ClCH=CHCH ₂ Cl CH ₂ =CClCH ₂ Cl	" " "
	CH ₂ CH=CHCH(CN)OSi(CH ₃) ₃	<i>n</i> -C ₈ H ₁₇ Br <i>i</i> -C ₈ H ₁₇ I (<i>E</i>)-CH ₂ CH=CHCH ₂ Br ^a	" " "
			"
	CH ₂ =CHCH(CN)OCH(OC ₂ H ₅)CH ₃ CH ₂ CH=CHCH(CN)OSi(CH ₃) ₃	<i>n</i> -C ₈ H ₁₇ Br C ₆ H ₅ CH ₂ Br C ₆ H ₅ (CH ₂) ₂ Br CH ₂ OSO ₂ C ₆ H ₄ CH ₃ -4 <i>n</i> -C ₈ H ₁₇ OSO ₂ C ₆ H ₄ CH ₃ -4 C ₆ H ₅ (CH ₂) ₂ Br	" " " " " "
C ₉	CH ₂ =C(CH ₃)CH(CN)OSi(CH ₃) ₃	CH ₂ Br ₂	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
		C ₂ H ₅ Br Br(CH ₂) ₂ Br <i>n</i> -C ₃ H ₇ Br	" " "

CYANOHYDRINS WITH ALKYL HALIDES

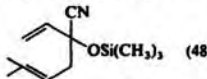
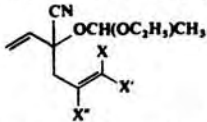
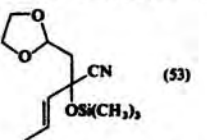
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF, HMPA, -78°	(CH ₃ O) ₂ C(C ₆ H ₁₇ - <i>n</i>)CN (55)	901
THF, -78°	CH ₂ =CHC(CH ₃)(CN)OSi(CH ₃) ₃ (77)	902,416
"	CH ₂ =CHC(C ₂ H ₅ - <i>n</i>)(CN)OSi(CH ₃) ₃ (58)	902,416
"	CH ₂ =CHC(CH ₂ CH=CH ₂)(CN)OSi(CH ₃) ₃ (79)	421
THF, HMPA, -78°	CH ₂ C(CH ₂ OCH ₃)(CN)OCH(OC ₂ H ₅)CH ₃ (71)	413
"	CH ₂ C(C ₂ H ₅ - <i>n</i>)(CN)OCH(OC ₂ H ₅)CH ₃ (80)	413
"	CH ₂ C(CH ₂ CH=CH ₂)(CN)OCH(OC ₂ H ₅)CH ₃ (76)	413
"	CH ₂ C(C ₆ H ₅ - <i>n</i>)(CN)OCH(OC ₂ H ₅)CH ₃ (80-85)	413
THF, -78°	 (48)	421
THF, HMPA, -78°	CH ₂ C(C ₂ H ₅ - <i>n</i>)(CN)OCH(OC ₂ H ₅)CH ₃ (80)	413
"	CH ₂ C(C ₆ H ₁₁ - <i>n</i>)(CN)OCH(OC ₂ H ₅)CH ₃ (80-85)	413
"	CH ₂ C(C ₆ H ₁₁)(CN)OCH(OC ₂ H ₅)CH ₃ (41)	413
"	CH ₂ C[(CH ₂) ₂ CH=CHC ₂ H ₅](CN)OCH(OC ₂ H ₅)CH ₃ (61)	413
"	CH ₂ C[CH ₂ CH(OC ₂ H ₅) ₂](CN)OCH(OC ₂ H ₅)CH ₃ (59)	413
"	CH ₂ C[(CH ₂) ₂ C ₆ H ₅](CN)OCH(OC ₂ H ₅)CH ₃ (84)	413
"	CH ₂ C(C ₁₀ H ₂₁ - <i>n</i>)(CN)OCH(OC ₂ H ₅)CH ₃ (80-85)	413
THF, -78°	CH ₂ CH=CHC(CH ₃)(CN)OSi(CH ₃) ₃ (87)	416,902
"	CH ₂ CH=CHC(C ₂ H ₅)(CN)OSi(CH ₃) ₃ (85)	416,902
"	CH ₂ CH=CHC[(CH ₂) ₂ Br](CN)OSi(CH ₃) ₃ (31)	416,902
"	CH ₂ CH=CHC(C ₂ H ₅ - <i>n</i>)(CN)OSi(CH ₃) ₃ (82)	416,902
"	CH ₂ CH=CHC(CH ₂ CH=CH ₂)(CN)OSi(CH ₃) ₃ (75)	416,421,902
"	CH ₂ CH=CHC[(CH ₂) ₂ Br](CN)OSi(CH ₃) ₃ (79)	416,902
"	CH ₂ =C(CH ₃)C(CH ₃)(CN)OSi(CH ₃) ₃ (80)	416,902
"	CH ₂ =C(CH ₃)C(C ₂ H ₅ - <i>n</i>)(CN)OSi(CH ₃) ₃ (67)	416,902
THF	CH ₂ =C(OCH ₃)C(CH ₃)(CN)OSi(CH ₃) ₃ (80)	902
"	CH ₂ =C(OCH ₃)C(C ₂ H ₅ - <i>n</i>)(CN)OSi(CH ₃) ₃ (75)	902
"	CH ₂ =C(OCH ₃)C(CH ₂ C ₆ H ₅)(CN)OSi(CH ₃) ₃ (80)	902
		
THF, HMPA	I X = X' = H, X' = Cl (39)	417,415
"	I X' = X'' = H, X = Cl (-)	417,415
"	I X = X' = H, X'' = Cl (38)	417
THF, -78°	CH ₂ CH=CHC(C ₆ H ₅ - <i>n</i>)(CN)OSi(CH ₃) ₃ (73)	416,902
"	CH ₂ CH=CHC(C ₆ H ₅ - <i>n</i>)(CN)OSi(CH ₃) ₃ (53)	902
"	CH ₂ CH=CHC(CH ₂ CH=CH ₂)(CN)OSi(CH ₃) ₃ (-)	421
	 (53)	416
THF, HMPA, -78°	CH ₂ =CHC(C ₆ H ₁₁ - <i>n</i>)(CN)OCH(OC ₂ H ₅)CH ₃ (75)	413
THF, -78°	CH ₂ CH=CHC(CH ₂ C ₆ H ₅)(CN)OSi(CH ₃) ₃ (76)	416,902
"	CH ₂ CH=CHC[(CH ₂) ₂ C ₆ H ₅](CN)OSi(CH ₃) ₃ (40-76)	416,902
"	CH ₂ CH=CHC(CH ₃)(CN)OSi(CH ₃) ₃ (82)	416,902
"	CH ₂ CH=CHC(C ₆ H ₅ - <i>n</i>)(CN)OSi(CH ₃) ₃ (62)	416,902
"	CH ₂ =C(CH ₃)C[(CH ₂) ₂ C ₆ H ₅](CN)OSi(CH ₃) ₃ (58)	416,902
-	C ₆ H ₅ C(CH ₂ Br)(OCH ₃)CN (70)	194
-	C ₆ H ₅ C(C ₂ H ₅)(OCH ₃)CN (75)	194
-	C ₆ H ₅ C[(CH ₂) ₂ Br](OCH ₃)CN (12)	194
-	C ₆ H ₅ C(C ₂ H ₅ - <i>n</i>)(OCH ₃)CN (73)	194

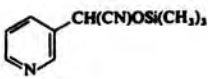
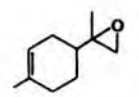
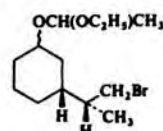
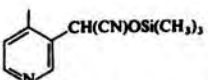
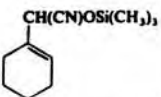
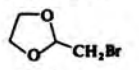


TABLE XII. ALKYLATION OF ANIONS OF PROTECTED

No. of C Atoms	Nucleophile	Electrophile	Base	
C ₉ (Contd.)	$(\text{CH}_3)_2\text{C}=\text{CHCH}(\text{CN})\text{OSi}(\text{CH}_3)_2$	<i>i</i> -C ₃ H ₇ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
		CH ₂ =CHCH ₂ Cl	"	
		CH ₃ I	LDA	
		<i>i</i> -C ₃ H ₇ I	"	
		CH ₃ I	"	
	C ₆ H ₅ CH(CN)OCH ₃	<i>i</i> -C ₃ H ₇ I	"	
		(CH ₃) ₂ C=CHCH ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	
	C ₁₀	$(\text{CH}_3)_2\text{C}=\text{CHCH}(\text{CN})\text{OSi}(\text{CH}_3)_2$	C ₆ H ₅ CH ₂ Cl	LDA
			C ₆ H ₅ (CH ₂) ₂ Br	"
		CH ₂ =CHCH(CN)OSi(C ₂ H ₅) ₂	CH ₃ I	"
(CH ₃) ₂ SiCH ₂ CH=C(CN)OSi(CH ₃) ₂		"	"	
CH ₃ (CH=CH) ₂ CH(CN)OSi(CH ₃) ₂ 1-Cyanoisochroman		CH ₃ I ^a	NaNH ₂	
		CH ₃ I	LDA	
		"	"	
C ₆ H ₅ CH(CN)OC ₂ H ₅ 4-ClC ₆ H ₄ CH(CN)OC ₂ H ₅ 1-Cyanoisochroman		C ₂ H ₅ I	<i>i</i> -C ₄ H ₉ OK	
CH ₃ (CH=CH) ₂ CH(CN)OSi(CH ₃) ₂		C ₂ H ₅ Br ^a	NaNH ₂	
		CH ₃ OCH ₂ Cl ^a CH ₃ SCH ₂ Cl ^a <i>i</i> -C ₃ H ₇ I	LDA	
	"	"		
1-Cyanoisochroman	<i>n</i> -C ₃ H ₇ Br ^a <i>i</i> -C ₃ H ₇ Br ^a C ₂ H ₅ OCH ₂ Cl ^a C ₂ H ₅ SCH ₂ Cl ^a	NaNH ₂ " " "		
	<i>i</i> -C ₃ H ₇ I	LDA		
	"	"		
	"	"		
	<i>n</i> -C ₄ H ₉ Br	"		
	Br(CH ₂) ₆ CO ₂ C ₂ H ₅	"		
<i>i</i> -C ₄ H ₉ CH(CN)OCH(OC ₂ H ₅)CH ₃	3-(Bromomethyl)furan	"		

CYANOHYDRINS WITH ALKYL HALIDES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	C ₆ H ₅ C(C ₂ H ₅ - <i>i</i>)(OCH ₃)CN (45)	194
THF, -78°	C ₆ H ₅ C(CH ₂ CH=CH ₂)(OCH ₃)CN (73)	194
"	(CH ₃) ₂ C=CHC(CH ₃)(CN)OSi(CH ₃) ₂ (88)	416,902
"	(CH ₃) ₂ C=CHC(C ₂ H ₅ - <i>i</i>)(CN)OSi(CH ₃) ₂ (84)	416,902
"	(2-C ₄ H ₉ O)COCH ₃ (92) ^b	428,430
"	(2-C ₄ H ₉ O)COC ₂ H ₅ - <i>i</i> (80) ^b	428
—	C ₆ H ₅ C[CH ₂ CH=C(CH ₃) ₂](OCH ₃)CN (78)	194
THF	C ₆ H ₅ C(CH ₂ C ₆ H ₅)(OCH ₃)CN (70)	194
THF, -78°	(CH ₃) ₂ C=CHC(CH ₃)(C ₆ H ₅)(CN)OSi(CH ₃) ₂ (84)	902
"	CH ₂ =CHC(CH ₃)(CN)OSi(C ₂ H ₅) ₂ , I. C ₂ H ₅ CH=C(CN)OSi(C ₂ H ₅) ₂ , II I:II = 95:5 (79)	902
"	(CH ₃) ₂ SiCH=CHC(CH ₃)(CN)OSi(CH ₃) ₂ , I. (CH ₃) ₂ SiCH(CH ₃)CH=C(CN)OSi(CH ₃) ₂ , II, I:II = 60:40 (77)	902
"	CH ₃ (CH=CH) ₂ C(C ₂ H ₅)(CN)OSi(CH ₃) ₂ (97)	416,902
C ₆ H ₆	1-Cyano-1-methylisochroman (21)	903
THF, -78°	2-C ₂ H ₄ NCOCH ₃ (80) ^b	428,430
"	4-C ₂ H ₄ NCOCH ₃ (84) ^b	429,430
THF	C ₆ H ₅ C(C ₂ H ₅)(OC ₂ H ₅)CN (63)	424
"	4-ClC ₆ H ₄ C(C ₂ H ₅)(OC ₂ H ₅)CN (51)	424
C ₆ H ₆	1-Cyano-1-ethylisochroman (35)	903
"	1-Cyano-1-(methoxymethyl)isochroman (26)	903
"	1-Cyano-1-(methylthiomethyl)isochroman (22)	903
THF, -78°	CH ₃ (CH=CH) ₂ C(C ₂ H ₅ - <i>i</i>)(CN)OSi(CH ₃) ₂ (94)	416,902
"		(98)
C ₆ H ₆	1-Cyano-1- <i>n</i> -propylisochroman (38)	903
"	1-Cyano-1-isopropylisochroman (11)	903
"	1-Cyano-1-(ethoxymethyl)isochroman (15)	903
"	1-Cyano-1-(ethylthiomethyl)isochroman (19)	903
THF, -78°	4-C ₂ H ₄ NCOC ₂ H ₅ - <i>i</i> (80) ^b	429,430
"	2-C ₂ H ₄ NCOC ₂ H ₅ - <i>i</i> (75) ^b	428,430
"	3-C ₂ H ₄ NCOC ₂ H ₅ - <i>i</i> (78) ^b	429,430
THF, HMPA, -78°	2-C ₂ H ₅ OCOC ₄ H ₉ - <i>n</i> (90) ^b	413
THF, HMPA, -65° to -75°		(-)
THF, HMPA, -78°		(38) ^b
		419

TABLE XII. ALKYLATION OF ANIONS OF PROTECTED

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₀ (Contd.)		C ₆ H ₅ CH ₂ Br	LDA
	(CH ₃) ₂ C=CHCH(CN)OCH(OC ₂ H ₅)CH ₃		"
	<i>i</i> -C ₄ H ₉ CH(CN)OCH(OC ₂ H ₅)CH ₃		"
C ₁₁	CH ₂ =C(CH ₃)CH(CN)OSi(CH ₃) ₃	CH ₃ I	"
	C ₆ H ₅ CH(CN)OSi(CH ₃) ₃	CH ₃ I	"
	C ₆ H ₅ CH(CN)OCH ₂ CH=CH ₂	(CH ₃ O) ₂ SO ₂	"
	C ₆ H ₅ CH(CN)OSi(CH ₃) ₃	C ₂ H ₅ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	C ₆ H ₅ CH(CN)OSi(CH ₃) ₃	C ₂ H ₅ I	LDA
	C ₆ H ₅ CH(CN)OSi(CH ₃) ₃	Br(CH ₂) ₂ Br	"
		CH ₃ I	"
	CH ₂ =C(CH ₃)CH(CN)OSi(C ₂ H ₅) ₂	<i>i</i> -C ₃ H ₇ I	"
	C ₆ H ₅ CH(CN)OSi(CH ₃) ₃	"	"
		CH ₂ =CHCH ₂ Br	"
		Br(CH ₂) ₂ Br	"
		C(CH ₃) ₂ Br	"
		CH ₂ =CHCH ₂ Br ^a	"
	<i>n</i> -C ₃ H ₇ CH(CN)OCH(OC ₂ H ₅)CH ₃	<i>n</i> -C ₄ H ₉ Br	"
	C ₆ H ₅ CH(CN)OSi(CH ₃) ₃	<i>n</i> -C ₄ H ₉ I	"
		<i>n</i> -C ₄ H ₉ Br	"
		<i>n</i> -C ₄ H ₉ Cl	"
		<i>i</i> -C ₄ H ₉ I	"
		(C ₂ H ₅ O) ₂ SO ₂	"
			"
		CH ₂ Br	"
			"
		CH ₂ I	"
			"
		C ₆ H ₁₁ Br	"
		(C ₂ H ₅ O) ₂ CHCH ₂ Br	"
		C ₆ H ₅ CH ₂ Br	"

CYANOHYDRINS WITH ALKYL HALIDES (Continued)

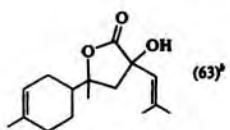
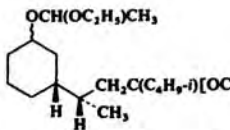
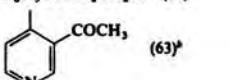
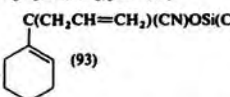

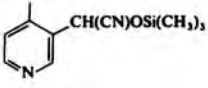
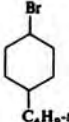

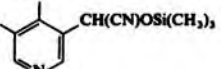
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF, -78°	3-C ₂ H ₅ NCOCH ₂ C ₆ H ₅ (84) ^b	429,430
THF, HMPA, -78°	 (63) ^b	418
THF, -78°	 (100)	904
"	CH ₂ =C(CH ₃)C(CH ₃)(CN)OSi(C ₂ H ₅) ₂ , I, C ₂ H ₅ C(CH ₃)=C(CN)OSi(C ₂ H ₅) ₂ , II I:II = 71:29 (90)	902
"	C ₆ H ₅ COCH ₂ (98) ^b	428,430
"	" (92) ^b	429,430
"	C ₆ H ₅ C(C ₂ H ₅)(CN)OCH ₂ CH=CH ₂ (44)	194
"	C ₆ H ₅ COC ₂ H ₅ (98) ^b	428,430
"	C ₆ H ₅ COCH ₂ CH ₂ Br (30) ^b	429
"	 (63) ^b	428,430
THF	CH ₂ =C(CH ₃)C(C ₃ H ₇ - <i>i</i>)(CN)OSi(C ₂ H ₅) ₂ , I, <i>i</i> -C ₃ H ₇ CH ₂ C(CH ₃)=C(CN)OSi(C ₂ H ₅) ₂ , II I:II = 95:5 (89)	902
THF, -78°	C ₆ H ₅ COC ₂ H ₅ - <i>i</i> (95) ^b	428,430
"	C ₆ H ₅ COCH ₂ CH=CH ₂ (96) ^b	429,430
"	C ₆ H ₅ CO(CH ₂) ₂ Br (80) ^b	429,430
"	C ₆ H ₅ CO(CH ₂) ₂ Cl (85) ^b	429,430
"	 (93)	421
THF, HMPA, -78°	<i>n</i> -C ₃ H ₇ , C(C ₄ H ₉ - <i>n</i>)(CN)OCH(OC ₂ H ₅)CH ₃ (70)	413
THF, -78°	C ₆ H ₅ COC ₆ H ₅ - <i>n</i> (74)	430,429
"	" (72) ^b	430,429
"	" (87) ^b	430,429
"	C ₆ H ₅ COC ₆ H ₅ - <i>t</i> (84) ^b	428
"	C ₆ H ₅ COC ₂ H ₅ (70) ^b	430,429
"	C ₆ H ₅ COCH ₂ CHO (60) ^b	430,429
"	CH ₂ COC ₆ H ₅	430
"	 (76) ^b	430
"	" (80) ^b	430
"	C ₆ H ₅ COC ₆ H ₁₁ (48) ^b	429,430
"	C ₆ H ₅ COCH ₂ CHO (20) ^b	430
"	C ₆ H ₅ COCH ₂ C ₆ H ₅ (96) ^b	428,430

TABLE XII. ALKYLATION OF ANIONS OF PROTECTED

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₁ (Contd.)		"	LDA
		3-(Chloromethyl)-4-methylpyridine	"
		C ₆ H ₅ CH(CN)OSi(CH ₃) ₃	C ₆ H ₅ (CH ₂) ₂ Br CH ₃ OSO ₂ C ₆ H ₄ CH ₃ -4 C ₂ H ₅ OSO ₂ C ₆ H ₄ CH ₃ -4 <i>i</i> -C ₃ H ₇ OSO ₂ C ₆ H ₄ CH ₃ -4
		 C ₆ H ₅ - <i>t</i>	"
C ₁₂	1-Cyano-4,4-dimethylisochroman	<i>n</i> -C ₆ H ₅ OSO ₂ C ₆ H ₄ CH ₃ -4	"
		CH ₃ I ^a C ₂ H ₅ Br ^a CH ₃ OCH ₂ Cl ^a CH ₃ SCH ₂ Cl ^a	NaNH ₂ " " "
	C ₆ H ₅ CH(CN)OCH(OC ₂ H ₅)CH ₃	<i>i</i> -C ₃ H ₇ Br <i>n</i> -C ₆ H ₅ Br	LDA "
		C ₆ H ₅ (CH ₂) ₂ Br <i>n</i> -C ₃ H ₇ Br ^a C ₂ H ₅ OCH ₂ Cl ^a C ₆ H ₅ CH ₂ Cl ^a	NaNH ₂ " " "
	1-Cyano-4,4-dimethylisochroman	<i>n</i> -C ₆ H ₅ Br	NaNH ₂
C ₁₃	C ₆ H ₅ CH=CHCH(CN)OSi(CH ₃) ₃ C ₆ H ₅ CH ₂ CH=C(CN)OSi(CH ₃) ₃	CH ₃ I	LDA
		"	"
	4-(CH ₃) ₂ NC H ₄ CH(CN)OSi(CH ₃) ₃ C ₆ H ₅ CH=CHCH(CN)OSi(CH ₃) ₃	" <i>i</i> -C ₃ H ₇ I C ₆ H ₅ CH ₂ Br	" " "
C ₁₄	 C ₆ H ₅ CH(CN)O C ₆ H ₄ - <i>n</i> C ₆ H ₅ CH(CN)OCH(OC ₄ H ₉ - <i>n</i>)CH ₃	<i>n</i> -C ₇ H ₁₅ Br	NaH
		CH ₂ Br ₂ ^a	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl
	C ₆ H ₅ CH(CN)OC ₆ H ₅	C ₂ H ₅ Br ^a CH ₂ Br ₂ C ₂ H ₅ Br Br(CH ₂) ₂ Br <i>n</i> -C ₃ H ₇ Br ^a	" " " " "
	C ₆ H ₅ CH(CN)OCH(OC ₄ H ₉ - <i>n</i>)CH ₃	CH ₂ =CHCH ₂ Cl	"
	C ₆ H ₅ CH(CN)OC ₆ H ₅	<i>n</i> -C ₃ H ₇ Br <i>i</i> -C ₃ H ₇ Br CH ₂ =CHCH ₂ Cl Br(CH ₂) ₂ Br (CH ₃) ₂ C=CHCH ₂ Cl	" " " " "
C ₁₅	C ₆ H ₅ CH(CN)OCH ₂ C ₆ H ₅	C ₂ H ₅ Br	"
C ₁₆	1,3-[CH(CN)OSi(CH ₃) ₃] ₂ C ₆ H ₄	CH ₃ I	LDA
		"	"

CYANOHYDRINS WITH ALKYL HALIDES (Continued)

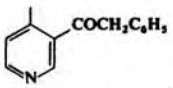
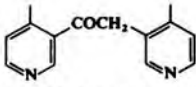
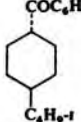
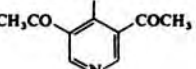
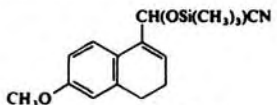
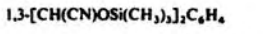
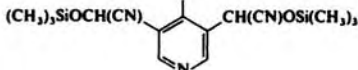
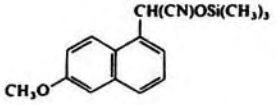
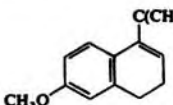

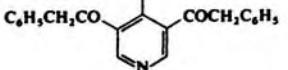
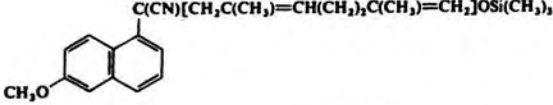
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF, -78°	 (59) ^b	428
"	 (64) ^b	428
"	C ₆ H ₅ CO(CH ₂) ₂ C ₆ H ₅ (62) ^b	429,430
"	C ₆ H ₅ COCH ₃ (80) ^b	430,429
"	C ₆ H ₅ COC ₂ H ₅ (85) ^b	430,429
DME, -78°	C ₆ H ₅ COC ₃ H ₇ - <i>i</i> (81) ^b	430
"	 (84) ^b	430
DME	C ₆ H ₅ COC ₄ H ₉ - <i>n</i> (91) ^b	430,429
C ₆ H ₆	1-Cyano-1,4,4-trimethylisochroman (39)	903
	1-Cyano-1-ethyl-4,4-dimethylisochroman (36)	903
	1-Cyano-1-(methoxymethyl)-4,4-dimethylisochroman (25)	903
	1-Cyano-4,4-dimethyl-1-(methylthiomethyl)-isochroman (12)	903
	C ₆ H ₅ COC ₃ H ₇ - <i>i</i> (94) ^b	413
THF, HMPA, -78°	C ₆ H ₅ COC ₄ H ₉ - <i>n</i> (94) ^b	413
	C ₆ H ₅ CO(CH ₂) ₂ C ₆ H ₅ (71) ^b	413
	1-Cyano-4,4-dimethyl-1- <i>n</i> -propylisochroman (25)	903
	1-Cyano-1-(ethoxymethyl)-4,4-dimethylisochroman (7)	903
	1-Benzyl-1-cyano-4,4-dimethylisochroman (35)	903
THF, -78°	C ₆ H ₅ CH=CHCOCH ₃ (72) ^b	428
	C ₆ H ₅ CH=CH(C(CH ₃) ₂ (CN)OSi(CH ₃) ₂) I, C ₆ H ₅ CH(CH ₃)CH=C(CN)OSi(CH ₃) ₂ II	902
	I:II = 70:30 (90)	
"	4-(CH ₃) ₂ NC ₆ H ₄ COCH ₃ (92) ^b	429,430
"	4-(CH ₃) ₂ NC ₆ H ₄ COC ₃ H ₇ - <i>i</i> (90) ^b	429,430
"	C ₆ H ₅ CH=CHCOCH ₂ C ₆ H ₅ (65) ^b	428
DMSO	C ₆ H ₅ COC ₃ H ₇ - <i>n</i> (83) ^b	414
	C ₆ H ₅ C(CN)OHCH ₂ Br (73) ^b	422
	C ₆ H ₅ C(CN)OHC ₂ H ₅ (81) ^b	422
	C ₆ H ₅ C(CH ₂ Br)(OC ₆ H ₅)CN (70)	194
	C ₆ H ₅ C(C ₂ H ₅)(OC ₆ H ₅)CN (63)	194
	C ₆ H ₅ C(CH ₂ CH ₂ Br)(OC ₆ H ₅)CN (64)	194
	C ₆ H ₅ COH(C ₃ H ₇ - <i>n</i>)CN (71) ^b	422
	C ₆ H ₅ COH(CH ₂ CH=CH ₂)CN (75) ^b	422
	C ₆ H ₅ C(C ₃ H ₇ - <i>n</i>)(OC ₆ H ₅)CN (66)	194
	C ₆ H ₅ C(C ₃ H ₇ - <i>i</i>)OC ₆ H ₅ CN (30)	194
	C ₆ H ₅ C(CH ₂ CH=CH ₂)(OC ₆ H ₅)CN (71)	194
	C ₆ H ₅ C[(CH ₂) ₂ Br](OC ₆ H ₅)CN (15)	194
	C ₆ H ₅ C[(CH ₂) ₂ Br](OC ₆ H ₅)CN (69)	194
	C ₆ H ₅ C(C ₂ H ₅)(OCH ₂ C ₆ H ₅)CN (71)	194
THF, -78°	1,3-(CH ₂ CO) ₂ C ₆ H ₄ (81) ^b	428,430
"	 (44) ^b	430

TABLE XII. ALKYLATION OF ANIONS OF PROTECTED

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₆ (Contd.)	 CH(OSi(CH ₃) ₃)CN CH ₃ O	CH ₂ =CHCH ₂ Br ^a	LDA
	 1,3-[CH(CN)OSi(CH ₃) ₃] ₂ C ₆ H ₄	C ₆ H ₅ CH ₂ Br	"
	 (CH ₃) ₃ SiOCH(CN)	"	"
	 CH(CN)OSi(CH ₃) ₃ CH ₃ O	(E)-CH ₂ =C(CH ₃)(CH ₂) ₂ CH=C(CH ₃)CH ₂ Cl	n-C ₄ H ₉ Li

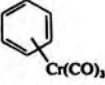
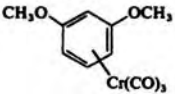

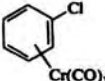
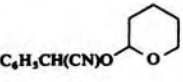
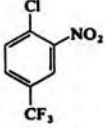
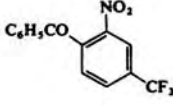
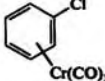
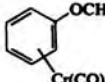
^a The precise leaving group in the alkylating agent was unspecified.

CYANOHYDRINS WITH ALKYL HALIDES (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF, -78°	 C(CH ₂ CH=CH ₂)(CN)OSi(CH ₃) ₃ CH ₃ O (83)	421
"	 1,3-C ₆ H ₄ (COCH ₂ C ₆ H ₅) ₂ (52)	430
"	 C ₆ H ₅ CH ₂ CO COCH ₂ C ₆ H ₅ (68)	430
"	 C(CN)[CH ₂ C(CH ₃)=CH(CH ₂) ₂ C(CH ₃)=CH ₂]OSi(CH ₃) ₃ CH ₃ O (58)	905

^a The initial product was hydrolyzed.

TABLE XIII. ARYLATION OF PROTECTED CYANOHYDRINS

No. of C atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉	C ₆ H ₅ CH(CN)OCH ₃	4-O ₂ NC ₆ H ₄ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	—	C ₆ H ₅ C(OCH ₃)(CN)C ₆ H ₄ NO ₂ -4 (42)	194
C ₉ -C ₁₀	<i>n</i> -C ₃ H ₇ CH(CN)OCH(OC ₂ H ₅)CH ₃		LDA	THF, 0°	C ₆ H ₅ COC ₃ H ₇ - <i>n</i> (90) ^a	146
	<i>n</i> -C ₄ H ₉ CH(CN)OCH(OC ₂ H ₅)CH ₃		"	THF, HMPA	3,5-(CH ₃ O) ₂ C ₆ H ₃ COC ₄ H ₉ - <i>n</i> (92) ^a	283,146
	<i>i</i> -C ₃ H ₇ CH(CN)OCH(OC ₂ H ₅)CH ₃		"	THF, 0°	C ₆ H ₅ COC ₃ H ₇ - <i>i</i> (88) ^a	146
C ₁₂	C ₆ H ₅ CH(CN)OCH(OC ₂ H ₅)CH ₃		"	THF	C ₆ H ₅ COC ₆ H ₅ (88) ^a	146
C ₁₃		4-FC ₆ H ₄ NO ₂	NaH	DMSO	C ₆ H ₅ COC ₆ H ₄ NO ₂ -4 (35) ^b	414
			"	"	 (42) ^b	414
	3,4-(CH ₂ O) ₂ C ₆ H ₃ CH(CN)OCH(OC ₂ H ₅)CH ₃		LDA	THF	3,4-(CH ₂ O) ₂ C ₆ H ₃ COC ₆ H ₅ (90) ^a	146
	C ₆ H ₅ CH ₂ CH(CN)OCH(OC ₂ H ₅)CH ₃		"	THF, HMPA	C ₆ H ₅ CH ₂ COC ₆ H ₄ OCH ₃ -3 (100) ^a	283
C ₁₄	C ₆ H ₅ CH(CN)OC ₆ H ₄ Cl ₂ -2,4 C ₆ H ₅ CH(OC ₆ H ₅)CN	C ₆ H ₅ NO ₂ 1-O ₂ NC ₁₀ H ₇	NaOH "	DMSO, 30° "	4-O ₂ NC ₆ H ₄ CH(C ₆ H ₅)CN (-) 4-O ₂ NC ₁₀ H ₇ CH(C ₆ H ₅)CN (77)	279 279

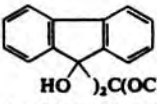

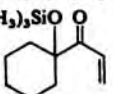

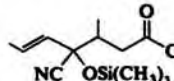

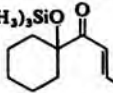
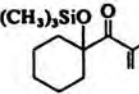
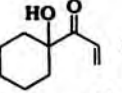
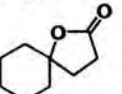

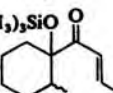

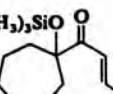
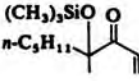
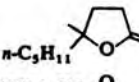

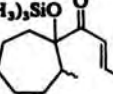
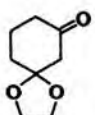
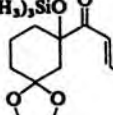
^a The initial product was treated with iodine followed by aqueous acid and base.

^b The initial product was hydrolyzed.

TABLE XIV. ACYLATION OF ANIONS OF PROTECTED CYANOHYDRINS

No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs
C ₁₀	1-Cyanoisochroman	ClCO ₂ CH ₃	C ₆ H ₅ Li	Dioxane-Et ₂ O	1-Carbomethoxy-1-cyanoisochroman (30)	903
	"	<i>t</i> -C ₄ H ₉ COCl	"	"	1-Cyano-1-pivaloylisochroman (26)	903
	"	(C ₂ H ₅) ₂ NCOCI	"	"	1-Cyano-1-(<i>N,N</i> -diethylcarbamoyl)isochroman (34)	903
	"	C ₆ H ₅ COCl	"	"	1-Benzoyl-1-cyanoisochroman (14)	903

TABLE XV. ADDITION OF ANIONS OF PROTECTED CYANOHYDRINS TO ALDEHYDES, KETONES, AND OLEFINS

No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₃	CH ₃ OCH ₂ CN	(C ₆ H ₅) ₂ CO	<i>n</i> -C ₄ H ₉ Li	THF, 0°	(C ₆ H ₅) ₂ COHCH(OCH ₃)CN (25)	336	
		9-Fluorenone	"	"	 (36)	336	
		4-CH ₃ C ₆ H ₄ COC ₆ H ₅	"	"	4-CH ₃ C ₆ H ₄ (C ₆ H ₅)COHCH(OCH ₃)CN (20)	336	
C ₇	CH ₂ =CHCH(CN)OSi(CH ₃) ₃		LDA	THF, -70° to -100°	 (30) ^r	449	
		<i>n</i> -C ₇ H ₁₁ CHO	"	THF, HMPA, -78°	CH ₃ COCHOHC ₇ H _{11-n} (50) ^r	446	
	CH ₃ CH(CN)OCH(OC ₂ H ₅)CH ₃		"	"	HO-COCH ₃ (68) ^r	446	
		C ₆ H ₅ CHO C ₆ H ₅ COC ₆ H ₅	"	"	CH ₃ COCHOHC ₆ H ₅ (82) ^r CH ₃ COC(C ₆ H ₅) ₂ OH (75) ^r	446 446	
C ₈	CH ₃ CH=CHCH(CN)OSi(CH ₃) ₃ C ₂ H ₅ CH(CN)OCH(OC ₂ H ₅)CH ₃	CH ₃ CHO	"	THF, -78°	CH ₃ CH=CHCOCH(CH ₃)OSi(CH ₃) ₃ (50-71) ^r	906	
		CH ₃ COCH ₃	"	THF, HMPA, -78°	C ₂ H ₅ COC(CH ₃) ₂ OSi(CH ₃) ₃ (42) ^r	910	
	CH ₃ CH=CHCH(CN)OSi(CH ₃) ₃	<i>t</i> -C ₄ H ₉ CHO	"	THF, -78°	 CH[OSi(CH ₃) ₃]C ₄ H _{9-t} (63) ^r	906	
			"	THF, -70° to -100°	 (64-68) ^r	449,45	
	CH ₂ =C(CH ₃)CH(CN)OSi(CH ₃) ₃	"	"	"	 (46) ^r	449	
		CH ₂ =CHCH(CN)OCH(OC ₂ H ₅)CH ₃	"	"	THF, -78°	 (72) ^r	449
	C ₆ H ₅ CHOHCN ^a C ₆ H ₅ CDOHCN ^b	C ₆ H ₅ CHO	KCN	C ₂ H ₅ OH	THF, -78° to 0°	 (60) ^r	449
		"	"	"	"	C ₆ H ₅ COCHOHC ₆ H ₅ (-) " (-)	432 432
	CH ₃ CH=CHCH(CN)OSi(CH ₃) ₃		LDA	"	THF, -70° to 100°	 (71) ^r	449,45
			"	"	"	 (64) ^r	449,45
CH ₂ =CHCH(CN)OCH(OC ₂ H ₅)CH ₃	<i>n</i> -C ₇ H ₁₁ COCH ₃	"	"	THF, -78°	 (76) ^r	449	
	"	"	"	THF, -78° to 0°	 (43) ^r	449	
CH ₃ CH=CHCH(CN)OSi(CH ₃) ₃		"	"	THF, -70° to -100°	 (44) ^r	449	
		"	"	"	 (54) ^r	449	

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TABLE XV. ADDITION OF ANIONS OF PROTECTED CYANOHYDRINS TO ALDEHYDES, KETONES, AND OLEFINS (Continued)

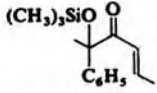
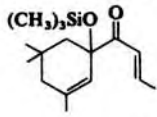
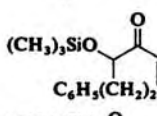
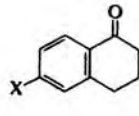
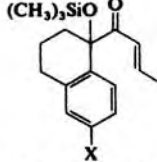
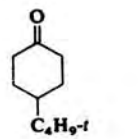
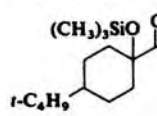
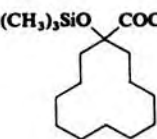
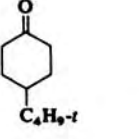
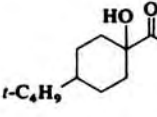
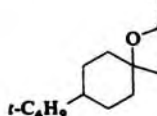
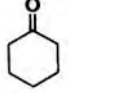
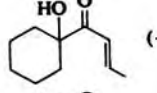
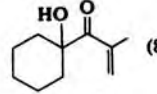
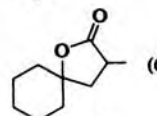
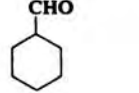
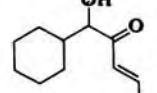
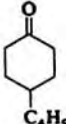
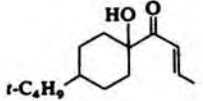

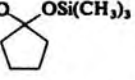

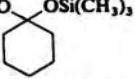
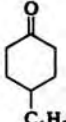
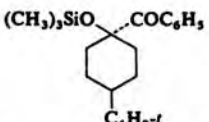

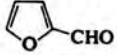
No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ (Contd.)		C ₆ H ₅ COCH ₃	LDA	THF, -70° to -100°	 (69)*	449,453,906
		Isophorone	"	"	 (53)*	449,453
		C ₆ H ₅ (CH ₂) ₂ CHO	"	"	 (47)*	449
			"	"	 I I X = H (78)* I X = OCH ₃ (89)*	449,453
			"	"	 (70)*	449,906
		Cyclododecanone	"	"	 (30)*	449
	CH ₂ =CHCH(CN)OCH(OC ₂ H ₅)CH ₃		"	THF, -78°	 (80)*	449
		"	"	THF, -78° to 0°	 (60)*	449
279	CH ₃ CH=CHCH(CN)OCH(OC ₂ H ₅)CH ₃		"	THF, 0°	 (-)*	449
	CH ₂ =C(CH ₃)CH(CN)OCH(OC ₂ H ₅)CH ₃	"	"	THF, -78°	 (83)*	449
		"	"	THF, -78° to 0°	 (65)*	449
	CH ₃ CH=CHCH(CN)OCH(OC ₂ H ₅)CH ₃		"	THF, 0°	 (69)*	449

TABLE XV. ADDITION OF ANIONS OF PROTECTED CYANOHYDRINS TO ALDEHYDES, KETONES, AND OLEFINS (Continued)

No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ (Contd.)			LDA	THF, 0°	 (56) ^f	449
280 C ₁₀	CH ₂ =CHCH(CN)OSi(CH ₃) ₃	CH ₃ COCH ₃	"	THF, -78°	CH ₂ =CHCOC(CH ₃) ₂ OSi(CH ₃) ₃ (76) ^a	906
C ₁₁	C ₆ H ₅ CH(CN)OSi(CH ₃) ₃	CH ₃ CHO	"	DME, -78°	C ₆ H ₅ COCH[OSi(CH ₃) ₃]CH ₃ (98) ^a	447,448
		C ₂ H ₅ CHO	"	"	C ₆ H ₅ COCH[OSi(CH ₃) ₃]C ₂ H ₅ (91) ^a	447,448
		CH ₃ COCH ₃	"	"	C ₆ H ₅ COC[OSi(CH ₃) ₃](CH ₃) ₂ (98) ^a	447,448
		<i>i</i> -C ₃ H ₇ CHO	"	"	C ₆ H ₅ COCH[OSi(CH ₃) ₃]C ₃ H ₇ - <i>i</i> (100) ^a	447,448
		<i>t</i> -C ₄ H ₉ CHO	"	"	C ₆ H ₅ COCH[OSi(CH ₃) ₃]C ₄ H ₉ - <i>t</i> (96) ^a	447,448
			"	"	 (98) ^a	447,448
			"	"	 (100) ^a	447,448
		CH ₂ =CH ₂ , PdCl ₂ (CH ₃ CN) ₂ , CO, CH ₃ OH	"	THF, HMPA	C ₆ H ₅ COCH ₂ CH ₂ CO ₂ CH ₃ (50) ^f	907
	CH ₂ =C(CH ₃)CH(CN)OSi(CH ₃) ₃	<i>t</i> -C ₄ H ₉ CHO	"	THF, -78°	CH ₂ =C(CH ₃)COCH(C ₄ H ₉ - <i>t</i>)OSi(CH ₃) ₃	906
	C ₆ H ₅ CH(CN)OSi(CH ₃) ₃	C ₆ H ₅ COCH ₃	"	DME, -78°	C ₆ H ₅ COC[OSi(CH ₃) ₃](CH ₃)C ₆ H ₅ (100) ^a	447,448
			"	"	 (98) ^a	448
		C ₆ H ₅ COC ₆ H ₅	"	"	C ₆ H ₅ COC[OSi(CH ₃) ₃](C ₆ H ₅) ₂ (98) ^a	447,448
C ₁₄		CH ₃ CHO	K ₂ CO ₃	<i>t</i> -C ₄ H ₉ OH	2-C ₆ H ₅ NCOCH(O ₂ CC ₆ H ₅)CH ₃ (72) ^d	443
C ₁₅	4-XC ₆ H ₄ CH(CN)O ₂ CC ₆ H ₅	"	"	"	4-XC ₆ H ₄ COCH(O ₂ CC ₆ H ₅)CH ₃ 1 ^e	443
			K ₂ CO ₃	<i>t</i> -C ₄ H ₉ OH	I X = H (59)	443
			KCN	DMF	I X = H (-)	444
			K ₂ CO ₃	<i>t</i> -C ₄ H ₉ OH	I X = NO ₂ (74)	443
			"	"	I X = Cl (18)	443
	C ₆ H ₅ CH(CN)O ₂ CC ₆ H ₅	C ₂ H ₅ CHO	"	"	C ₆ H ₅ COCH(O ₂ CC ₆ H ₅)C ₂ H ₅ (46) ^d	443
		<i>i</i> -C ₃ H ₇ CHO	"	"	C ₆ H ₅ COCH(O ₂ CC ₆ H ₅)C ₃ H ₇ - <i>i</i> (37) ^d	443
281 C ₁₆	4-XC ₆ H ₄ CH(CN)O ₂ CC ₆ H ₅		KCN	DMF	C ₆ H ₅ COCH(C ₄ H ₅ O-2)O ₂ CC ₆ H ₅ (-) ^f	444
		C ₆ H ₅ CHO	"	"	C ₆ H ₅ COCH(C ₆ H ₅)O ₂ CC ₆ H ₅ (-) ^f	444
		CH ₃ CHO	K ₂ CO ₃	<i>t</i> -C ₄ H ₉ OH	4-XC ₆ H ₄ COCH(O ₂ CC ₆ H ₅)CH ₃ 1 ^e	443
					I X = OCH ₃ (14)	
					I X = CN (52)	


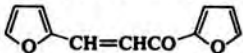



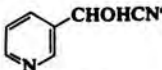

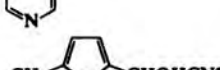
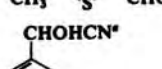
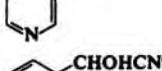

^a The initial product underwent an intramolecular 1,4-*O*-trimethylsilyl group migration and expelled cyanide.

^b The cyanohydrin was generated *in situ* from the corresponding aldehyde.

^c The initial product was hydrolyzed.

^d The initial product underwent an intramolecular benzoyl group migration.

TABLE XVI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF ANIONS OF

No. of C Atoms	Nucleophile	Electrophile	Base
C ₆	2-Furylglycolonitrile ^a	CH ₂ =CHCN	NaCN
	2-Thienylglycolonitrile ^a	"	"
	2-Furylglycolonitrile ^a	CH ₃ CH=CHCN	"
		CH ₂ =C(CH ₃)CN	"
	2-Thienylglycolonitrile ^a	CH ₂ =CHCOCH ₃	"
		CH ₃ CH=CHCN	"
		CH ₂ =CHCO ₂ C ₂ H ₅	"
		CH ₃ CH=CHCO ₂ C ₂ H ₅	"
		CH ₂ =CHCO- 	"
	2-Furylglycolonitrile ^a	C ₆ H ₅ CH=CHCN	"
		C ₆ H ₅ CH=CHCN	"
		C ₆ H ₅ CH=CHCO ₂ CH ₃	"
		C ₆ H ₅ CH=CHCOCH ₃	"
		 -CH=CHCO- 	"
	 -CH=CHCOC ₆ H ₅	"	
2-Thienylglycolonitrile ^a	C ₆ H ₅ CH=CHCOC ₆ H ₅	"	
	C ₆ H ₅ CH=CHCOCH ₃	"	
	C ₆ H ₅ CH=CHCO- 	"	
	C ₆ H ₅ CH=CHCOC ₆ H ₅	"	
C ₇		CH ₂ =CHCN	"
		CH ₂ =CHCN	"
		"	"
		CH ₂ =CHCOCH ₃	"
		"	"
		CH ₂ =CHCO ₂ C ₂ H ₅	"
	CH ₃ CH(CN)OCH(OC ₂ H ₅)CH ₃		

PROTECTED CYANOHYDRINS TO VARIOUS MICHAEL ACCEPTORS

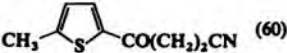
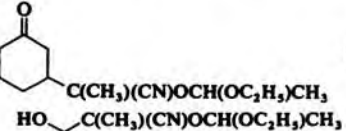
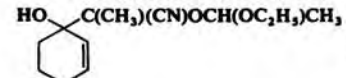



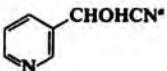
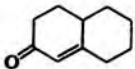

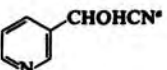
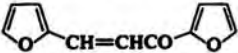
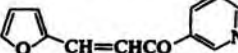
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
DMF or DMSO	(2-C ₄ H ₉ O)CO(CH ₂) ₂ CN (63-68)	442,434,435,437,440
DMF	(2-C ₄ H ₉ S)CO(CH ₂) ₂ CN (85)	440,434,435,437,438
"	(2-C ₄ H ₉ O)COCH(CH ₃)CH ₂ CN (73)	442,437
"	(2-C ₄ H ₉ O)COCH ₂ CH(CH ₃)CN (62)	437
"	(2-C ₄ H ₉ S)CO(CH ₂) ₂ COCH ₃ (80)	438
"	(2-C ₄ H ₉ S)COCH(CH ₃)CH ₂ CN (76)	438,437
"	(2-C ₄ H ₉ S)CO(CH ₂) ₂ CO ₂ C ₂ H ₅ (50)	439,437
"	(2-C ₄ H ₉ S)COCH(CH ₃)CH ₂ CO ₂ C ₂ H ₅ (54)	439,437
"	(2-C ₄ H ₉ S)CO(CH ₂) ₂ CO(C ₄ H ₉ S-2) (75)	438
"	(2-C ₄ H ₉ S)COCH(C ₆ H ₅)CH ₂ CN (71)	438,437
"	(2-C ₄ H ₉ O)COCH(C ₆ H ₅)CH ₂ CN (68)	442,437
DMF or DMSO	(2-C ₄ H ₉ O)COCH(C ₆ H ₅)CH ₂ CO ₂ CH ₃ (44)	434
DMF	(2-C ₄ H ₉ O)COCH(C ₆ H ₅)CH ₂ COCH ₃ (72)	436,437,440
"	(2-C ₄ H ₉ O)COCH(C ₄ H ₉ O-2)CH ₂ CO(C ₄ H ₉ O-2) (45)	441,437
"	(2-C ₄ H ₉ O)COCH(C ₄ H ₉ O-2)CH ₂ COC ₆ H ₅ (61)	441,437
"	(2-C ₄ H ₉ O)COCH(C ₆ H ₅)CH ₂ COC ₆ H ₅ (93)	436,434,437,440
"	(2-C ₄ H ₉ S)COCH(C ₆ H ₅)CH ₂ COCH ₃ (77)	438
"	(2-C ₄ H ₉ S)COCH(C ₆ H ₅)CH ₂ CO(C ₄ H ₉ S-2) (80)	438,437
"	(2-C ₄ H ₉ S)COCH(C ₆ H ₅)CH ₂ COC ₆ H ₅ (90)	438,437
"	(3-C ₄ H ₉ N)CO(CH ₂) ₂ CN (89)	440,434,435,437
"	(4-C ₄ H ₉ N)CO(CH ₂) ₂ CN (71)	440,434,435,437
"	 (60)	438,437
"	(4-C ₄ H ₉ N)CO(CH ₂) ₂ COCH ₃ (70)	436,437
"	(3-C ₄ H ₉ N)CO(CH ₂) ₂ COCH ₃ (88)	436,437
"	(3-C ₄ H ₉ N)CO(CH ₂) ₂ CO ₂ C ₂ H ₅ (37)	439,437
	 I,	
	 II	

TABLE XVI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF ANIONS OF

No. of C Atoms	Nucleophile	Electrophile	Base
C ₇ (Contd.)	CH ₃ CH(CN)OCH(OC ₂ H ₅)CH ₃		LDA
	CH ₃ CH(CN)OCH(OC ₂ H ₅)CH ₃		"
			"
		C ₆ H ₅ CH=CHNO ₂	"
		Isophorone	"
		CH ₂ =CHCOC ₆ H ₅	NaCN
	CH ₃ CH(CN)OCH(OC ₂ H ₅)CH ₃		LDA
		C ₆ H ₅ CH=CHCOC ₆ H ₅	NaCN
		C ₆ H ₅ COCH ₂ CH ₂ N(CH ₃) ₂	"
			"
			"

PROTECTED CYANOHYDRINS TO VARIOUS MICHAEL ACCEPTORS (Continued)









Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF, HMPA, -78°	I:II = 40:60 (-)	450
"	I:II = 50:50 (75)	446
THF, HMPA, -70°	I:II = 20:80 (>95)	908
THF, HMPA, -78°	HO-C(CH ₃)(CN)OCH(OC ₂ H ₅)CH ₃  I (90)	450
-	C(CH ₃)(CN)OCH(OC ₂ H ₅)CH ₃  II (70, I:II = 90:10)	446
THF, HMPA, -78°	C(CH ₃)(CN)OCH(OC ₂ H ₅)CH ₃  III	450
"	HO-C(CH ₃)(CN)OCH(OC ₂ H ₅)CH ₃  IV III:IV = 6:1 (-)	
"	CH ₃ C[CH(C ₆ H ₅)CH ₂ NO ₂](CN)OCH(OC ₂ H ₅)CH ₃ (55-85)	909
THF, HMPA, -70° to 0°	 I, C(CH ₃)(CN)OCH(OC ₂ H ₅)CH ₃	908
	 II, C(CH ₃)(CN)OCH(OC ₂ H ₅)CH ₃ I:II = 80:20 (>95)	
DMF	(3-C ₅ H ₄ N)CO(CH ₂) ₂ COC ₆ H ₅ (80)	436,437
THF, HMPA, -70°	 I, C(CH ₃)(CN)OCH(OC ₂ H ₅)CH ₃	908
	 II, C(CH ₃)(CN)OCH(OC ₂ H ₅)CH ₃ I:II = 50:50 (>95)	
DMF	(2-C ₅ H ₄ N)COCH(C ₆ H ₅)CH ₂ COC ₆ H ₅ (91)	436
"	(3-C ₅ H ₄ N)CO(CH ₂) ₂ COC ₆ H ₅ (35)	440
"	(3-C ₅ H ₄ N)COCH(C ₄ H ₉ O-2)CH ₂ CO(C ₄ H ₉ O-2) (88)	441,437
"	(3-C ₅ H ₄ N)COCH(C ₄ H ₉ O-2)CH ₂ CO(C ₄ H ₉ N-3) (56)	441

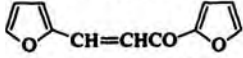
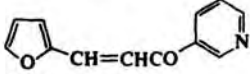
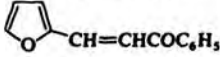
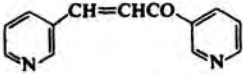
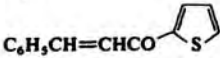
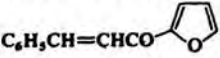
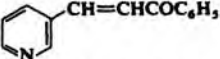
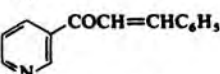
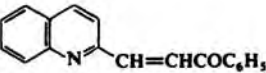


TABLE XVI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF ANIONS OF

No. of C Atoms	Nucleophile	Electrophile	Base
C ₇ (Contd.)			NaCN
			"
			"
			"
			"
C ₈			"
			"
		CH ₂ =CHCN	"
		"	"
		"	"
		CH ₂ =C(CH ₃)CN	"
		CH ₃ CH=CHCN	"
		CH ₂ =CHCOCH ₃	"
		"	"
		CH ₂ =CHCO ₂ C ₂ H ₅	"
		CH ₃ CH=CHCO ₂ CH ₃	"
		CH ₂ =CHCO ₂ C ₂ H ₅	"
		CH ₂ =C(CH ₃)CO ₂ CH ₃	"
		(CH ₃) ₂ C=CHCOCH ₃	LDA
		"	"
	"		
	CH ₃ CH=CHCO ₂ C ₂ H ₅	NaCN	
	"	"	
	CH ₂ =C(CH ₃)CO ₂ C ₂ H ₅	"	
	CH ₃ CH=CHCO ₂ C ₂ H ₅ -i	"	
	"	"	
	CH ₃ CH=CHCO ₂ C ₄ H ₉ -i	"	
	(Z)-C ₂ H ₅ O ₂ CCH=CHCO ₂ C ₂ H ₅	"	
	"	"	
	CH ₃ CH=CHCO ₂ C ₄ H ₉ -i	"	
	"	"	
CH ₃ CH=CHCH(CN)OSi(CH ₃) ₃	Isophorone	LDA	
	C ₆ H ₅ COCH=CH ₂	NaCN	
	C ₆ H ₅ CH=CHCN	"	
	C ₆ H ₅ CH=CHCOCH ₃	"	

PROTECTED CYANOHYDRINS TO VARIOUS MICHAEL ACCEPTORS (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
DMF	(3-C ₂ H ₄ N)COCH(C ₆ H ₅)CH ₂ CO(C ₄ H ₉ O-2) (80)	441,437	
"	(3-C ₂ H ₄ N)COCH(C ₄ H ₉ O-2)CH ₂ COC ₆ H ₅ (73)	437,441	
"	(3-C ₂ H ₄ N)COCH(C ₂ H ₄ N-3)CH ₂ CO(C ₂ H ₄ N-3) (74)	441,437	
"	(3-C ₂ H ₄ N)COCH(C ₂ H ₄ N-3)CH ₂ COC ₆ H ₅ (83)	441,437	
"	(3-C ₂ H ₄ N)COCH(C ₆ H ₅)CH ₂ CO(C ₂ H ₄ N-3) (72)	441,437	
DMF or DMSO	(2-C ₂ H ₄ N)COCH(C ₆ H ₅)CH ₂ COC ₆ H ₅ (91)	437,434	
DMF	(2-C ₂ H ₄ N)COCH(C ₆ H ₅ N-2)CH ₂ COC ₆ H ₅ (63)	441	
"	C ₆ H ₅ CO(CH ₂) ₂ CN (80)	435,437,440	
"	4-ClC ₆ H ₄ CO(CH ₂) ₂ CN (89-91)	440,435,437	
"	4-BrC ₆ H ₄ CO(CH ₂) ₂ CN (81)	440,435,437	
"	C ₆ H ₅ COCH ₂ CH(CH ₃)CN (73)	440,435,437	
"	C ₆ H ₅ COCH(CH ₃)CH ₂ CN (71)	440,435,437	
"	C ₆ H ₅ CO(CH ₂) ₂ COCH ₃ (82)	436,437,440	
"	4-ClC ₆ H ₄ CO(CH ₂) ₂ COCH ₃ (98)	436,437,440	
"	C ₆ H ₅ CO(CH ₂) ₂ CO ₂ C ₂ H ₅ (55)	439,437	
"	4-ClC ₆ H ₄ COCH(CH ₃)CH ₂ CO ₂ CH ₃ (35)	439,437	
"	4-ClC ₆ H ₄ CO(CH ₂) ₂ CO ₂ C ₂ H ₅ (68)	439,437	
"	4-ClC ₆ H ₄ COCH ₂ CH(CH ₃)CO ₂ CH ₃ (34)	437	
THF	(CH ₃) ₂ C=CHC(CH ₃)[OSi(CH ₃) ₃]COCH=CHCH ₃ (74)	906	
Et ₂ O	CH ₃ COCH ₂ C(CH ₃) ₂ C(CH=CHCH ₃)(CN)OSi(CH ₃) ₃ (25-60)	906	
THF		906	
DMF	C ₆ H ₅ COCH(CH ₃)CH ₂ CO ₂ C ₂ H ₅ (36)	440,439	
"	4-ClC ₆ H ₄ COCH(CH ₃)CH ₂ CO ₂ C ₂ H ₅ (56)	440,437,439	
"	4-ClC ₆ H ₄ COCH ₂ CH(CH ₃)CO ₂ C ₂ H ₅ (34)	439	
"	C ₆ H ₅ COCH(CH ₃)CH ₂ CO ₂ C ₃ H ₇ -i (40)	439,437	
"	4-ClC ₆ H ₄ COCH(CH ₃)CH ₂ CO ₂ C ₃ H ₇ -i (49)	437,439	
"	C ₆ H ₅ COCH(CH ₃)CH ₂ CO ₂ C ₄ H ₉ -i (52)	439,437	
"	C ₆ H ₅ COCH(CO ₂ C ₂ H ₅)CH ₂ CO ₂ C ₂ H ₅ (33)	440	
"	4-ClC ₆ H ₄ COCH(CO ₂ C ₂ H ₅)CH ₂ CO ₂ C ₂ H ₅ (35)	440	
"	4-ClC ₆ H ₄ COCH(CH ₃)CH ₂ CO ₂ C ₄ H ₉ -i (64)	439,437	
THF	(CH ₃) ₃ SiO-COCH=CHCH ₃ 	(53)	906
DMF	(C ₆ H ₅ COCH ₂) ₂ (66)	440	
"	C ₆ H ₅ COCH(C ₆ H ₅)CH ₂ CN (80)	440,435,437	
"	C ₆ H ₅ COCH(C ₆ H ₅)CH ₂ COCH ₃ (80)	436,437,440	

TABLE XVI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF ANIONS OF

No. of C Atoms	Nucleophile	Electrophile	Base
C ₈ (Contd.)	C ₆ H ₅ CHOHCN*	C ₆ H ₅ CN=CHCOCH ₃	NaCN or KCN
	4-ClC ₆ H ₄ CHOHCN*	"	NaCN
	C ₆ H ₅ CHOHCN*	C ₆ H ₅ CH=CHCO ₂ C ₂ H ₅	"
		C ₆ H ₅ COCH ₂ CH ₂ N(CH ₃) ₂	"
			"
	4-ClC ₆ H ₄ CHOHCN*	C ₆ H ₅ CH=CHCO ₂ C ₂ H ₅	"
	C ₆ H ₅ CHOHCN*		"
			"
			"
			"
			"
	4-ClC ₆ H ₄ CHOHCN*	C ₆ H ₅ CH=CHCO ₂ C ₄ H ₉ -t	"
	C ₆ H ₅ CHOHCN*		"
			"
	4-ClC ₆ H ₄ CHOHCN*	C ₆ H ₅ CH=CHCO ₂ C ₆ H ₅	"
C ₆ H ₅ CHOHCN*		"	
C ₉	3-CH ₃ C ₆ H ₄ CHOHCN*	CH ₂ =CHCN	"
	3-CH ₃ OC ₆ H ₄ CHOHCN*	"	"
	4-CH ₃ C ₆ H ₄ CHOHCN*	"	"
	4-CH ₃ OC ₆ H ₄ CHOHCN*	"	"
	(CH ₃) ₂ C=CHCH(CN)OSi(CH ₃) ₃	CH ₂ =CHCO ₂ C ₂ H ₅	LDA
	CH ₃ CH=CHCH(CN)OCH(OC ₂ H ₅)CH ₃		"
	(CH ₃) ₂ C=CHCH(CN)OSi(CH ₃) ₃ CH ₃ CH=CHCH(CN)OCH(OC ₂ H ₅)CH ₃	CH ₃ CH=CHCO ₂ C ₂ H ₅ (CH ₃) ₂ C=CHCOCH ₃	"
		"	

PROTECTED CYANOHYDRINS TO VARIOUS MICHAEL ACCEPTORS (Continued)


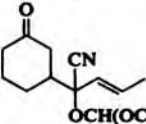
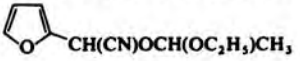





Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
DMSO	" (69)	440
DMF	4-ClC ₆ H ₄ COCH(C ₆ H ₅)CH ₂ COCH ₃ (98)	436,437,440
"	C ₆ H ₅ COCH(C ₆ H ₅)CH ₂ CO ₂ C ₂ H ₅ (54)	437,440
"	(C ₆ H ₅ COCH ₂) ₂ (61)	440
"	C ₆ H ₅ COCH(C ₄ H ₉ O-2)CH ₂ CO(C ₄ H ₉ O-2) (75)	441
"	4-ClC ₆ H ₄ COCH(C ₆ H ₅)CH ₂ CO ₂ C ₂ H ₅ (54)	439
"	C ₆ H ₅ COCH(C ₄ H ₉ O-2)CH ₂ CO(C ₃ H ₇ N-3) (53)	441
"	C ₆ H ₅ COCH(C ₄ H ₉ O-2)CH ₂ COC ₆ H ₅ (73)	441,437
"	C ₆ H ₅ COCH(C ₃ H ₇ N-3)CH ₂ CO(C ₃ H ₇ N-3) (48)	441,437
"	C ₆ H ₅ COCH(C ₆ H ₅)CH ₂ CO(C ₄ H ₉ S-2) (75)	441,437
"	C ₆ H ₅ COCH(C ₆ H ₅)CH ₂ CO(C ₄ H ₉ O-2) (78)	441
"	4-ClC ₆ H ₄ COCH(C ₆ H ₅)CH ₂ CO ₂ C ₄ H ₉ -t (60)	439,437
"	C ₆ H ₅ COCH(C ₃ H ₇ -3)CH ₂ COC ₆ H ₅ (87)	441,437
"	C ₆ H ₅ COCH(C ₆ H ₅)CH ₂ CO(C ₃ H ₇ N-3) (65)	441
"	C ₆ H ₅ COCH(C ₆ H ₅)CH ₂ COC ₆ H ₅ (93)	436,437
"	4-ClC ₆ H ₄ COCH(C ₆ H ₅)CH ₂ COC ₆ H ₅ (98)	436,437,440
"	C ₆ H ₅ COCH(C ₆ H ₅ N-2)CH ₂ COC ₆ H ₅ (48)	441
"	3-CH ₃ C ₆ H ₄ CO(CH ₂) ₂ CN (47)	437
"	3-CH ₃ OC ₆ H ₄ CO(CH ₂) ₂ CN (83)	437
"	4-CH ₃ C ₆ H ₄ CO(CH ₂) ₂ CN (43-70)	440,437
"	4-CH ₃ OC ₆ H ₄ CO(CH ₂) ₂ CN (54-60)	440,437
THF, -78°	(CH ₃) ₂ C=CHC[(CH ₂) ₂ CO ₂ C ₂ H ₅](CN)OSi(CH ₃) ₃ (15)	906
THF, HMPA, -78°	 (71)	450,446
THF	(CH ₃) ₂ C=CHC[CH(CH ₃)CH ₂ CO ₂ C ₂ H ₅](CN)OSi(CH ₃) ₃ (76)	906
THF, HMPA, -78°	CH ₃ CH=CHC[C(CH ₃) ₂ CH ₂ COCH ₃](CN)OCH(OC ₂ H ₅)CH ₃ (70-80)	911
"	 (77)	450,446

TABLE XVI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF ANIONS OF

No. of C Atoms	Nucleophile	Electrophile	Base
C ₉ (Contd.)	(CH ₃) ₂ C=CHCH(CN)OSi(CH ₃) ₃	ClCH ₂ CH=C(CH ₃)CO ₂ C ₂ H ₅	LDA
	CH ₃ CH=CHCH(CN)OCH(OC ₂ H ₅)CH ₃	C ₆ H ₅ CH=CHNO ₂	"
	(CH ₃) ₂ C=CHCH(CN)OSi(CH ₃) ₃	C ₆ H ₅ CH=CHCO ₂ C ₂ H ₅	"
	CH ₃ CH=CHCH(CN)OCH(OC ₂ H ₅)CH ₃	C ₆ H ₅ CH=CHCO ₂ C ₂ H ₅	"
C ₁₀	<i>n</i> -C ₄ H ₉ CH(CN)OCH(OC ₂ H ₅)CH ₃	C ₆ H ₅ CH=CHNO ₂	"
		"	"
	<i>i</i> -C ₄ H ₉ CH(CN)OCH(OC ₂ H ₅)CH ₃	(<i>E</i>)-CH ₂ =C(CH ₃)CH=CHS(O)C ₆ H ₅	"
C ₁₁	<i>n</i> -C ₅ H ₁₁ CH(CN)OCH(OC ₂ H ₅)CH ₃		"
	C ₆ H ₅ CH(CN)OSi(CH ₃) ₃	(CH ₃) ₂ C=CHCOCH ₃	"
			"
	4-ClC ₆ H ₄ CH(CN)OSi(CH ₃) ₃	CH ₃ CH=CHCO ₂ C ₂ H ₅ (CH ₃) ₂ C=CHCO ₂ CH ₃ (CH ₃) ₂ C=CHCOCH ₃	"
	C ₆ H ₅ CH(CN)OSi(CH ₃) ₃		"
			"
			"

PROTECTED CYANOHYDRINS TO VARIOUS MICHAEL ACCEPTORS (Continued)

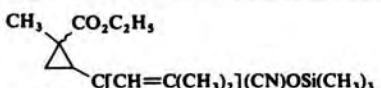
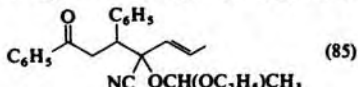
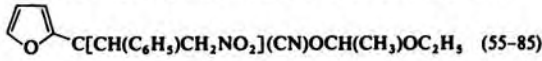
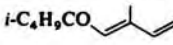
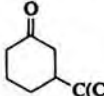
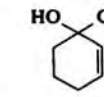
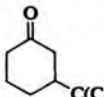
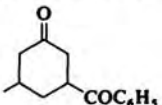
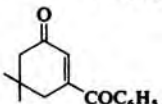
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF	 (71)	906
THF, HMPA, -78°	CH ₃ CH=CHC[CH(C ₆ H ₅)CH ₂ NO ₂](CN)OCH(OC ₂ H ₅)CH ₃ (55-85)	909
THF	(CH ₃) ₂ C=CHC(CN)[OSi(CH ₃) ₃]CH(C ₆ H ₅)CH ₂ CO ₂ C ₂ H ₅ (59)	906
THF, HMPA, -78°	 (85)	450,446
"	<i>n</i> -C ₄ H ₉ C[CH(C ₆ H ₅)CH ₂ NO ₂](CN)OCH(OC ₂ H ₅)CH ₃ (55-85)	909
"	 (55-85)	909
THF, -78°	<i>i</i> -C ₄ H ₉ CO-  (50, <i>E</i> : <i>Z</i> = 55:45) ^b	458
THF, HMPA, -78°	 I, C(C ₂ H ₁₁ - <i>n</i>)(CN)OCH(OC ₂ H ₅)CH ₃ HO-  II, (-, ratio I:II = 2.7:1)	450
"	C ₆ H ₅ COC(CH ₃)[OSi(CH ₃) ₃]CH=C(CH ₃) ₂ I, C ₆ H ₅ C(CN)[OSi(CH ₃) ₃]C(CH ₃) ₂ CH ₂ COCH ₃ II	
DME	I:II = 78:22 (92)	912
Et ₂ O	I:II = 0:100 (84)	912
Et ₂ O, -78°	 (96)	913
THF or Et ₂ O	C ₆ H ₅ COCH(CH ₃)CH ₂ CO ₂ C ₂ H ₅ (65) ^b	913
"	C ₆ H ₅ COC(CH ₃) ₂ CH ₂ CO ₂ CH ₃ (81) ^b	913
"	4-ClC ₆ H ₄ COC(CH ₃)[OSi(CH ₃) ₃]CH=C(CH ₃) ₂ I, 4-ClC ₆ H ₄ C(CN)[OSi(CH ₃) ₃]C(CH ₃) ₂ CH ₂ COCH ₃ II	
DME	I:II = 62:38 (100)	912
Et ₂ O	I:II = 0:100 (98)	912
Et ₂ O, -78°	 (83) ^b	913
"	 (40) ^b	913
"	" (90) ^b	913



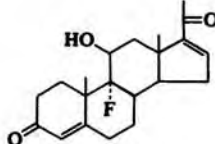
TABLE XVI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF ANIONS OF

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₁ (Contd.)	C ₆ H ₅ CH(CN)OSi(CH ₃) ₃		LDA
			"
			"
		(E)-C ₆ H ₅ CH=CHCOCH ₃	"
C ₁₂	C ₆ H ₅ CH(CN)OCH(OC ₂ H ₅)CH ₃		"
		CHOHCN*	"
	C ₆ H ₅ CH(CN)OCH(OC ₂ H ₅)CH ₃	CH ₂ =CHCHO	"
		CH ₂ =CHCN	NaCN
	4-CF ₃ C ₆ H ₄ CH(CN)OSi(CH ₃) ₃	(CH ₃) ₂ C=CHCOCH ₃	LDA
			"
	4-CH ₃ OC ₆ H ₄ CH(CN)OSi(CH ₃) ₃	(CH ₃) ₂ C=CHCOCH ₃	"
		"	"
4-NCC ₆ H ₄ CH(CN)OSi(CH ₃) ₃	"	"	
	"	"	
C ₆ H ₅ CH(CN)OCH(OC ₂ H ₅)CH ₃	C ₆ H ₅ CH=CHNO ₂	"	
	Isophorone	"	
			"

PROTECTED CYANOHYDRINS TO VARIOUS MICHAEL ACCEPTORS (Continued)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₂ O, -78°	 C(C ₆ H ₅)(CN)OSi(CH ₃) ₃ (95)	913
"	 COC ₆ H ₅ (45) ^a	913
"	 COC ₆ H ₅ (20) ^a	913
"	C ₆ H ₅ C(CN)[OSi(CH ₃) ₃]CH(C ₆ H ₅)CH ₂ COCH ₃ (87)	913
"	 C(C ₆ H ₅)(CN)OSi(CH ₃) ₃ (95)	913
THF or Et ₂ O	C ₆ H ₅ COCH(C ₆ H ₅)CH ₂ CO ₂ H (75)	913
-	C ₆ H ₅ C(CN)[(CH ₃) ₂ CHO]OCH(OC ₂ H ₅)CH ₃ (90)	446
DMF	2-C ₁₀ H ₇ CO(CH ₂) ₂ CN (81)	440,436,437
-	C ₆ H ₅ C(CN)[OCH(OC ₂ H ₅)CH ₃]C(CH ₃) ₂ CH ₂ COCH ₃ (88)	446
THF	 C(C ₆ H ₅)(CN)OCH(OC ₂ H ₅)CH ₃ (>95)	908
DME Et ₂ O	4-CF ₃ C ₆ H ₄ COC(CH ₃) ₂ [OSi(CH ₃) ₃]CH=C(CH ₃) ₂ I, 4-CF ₃ C ₆ H ₄ C(CN)[OSi(CH ₃) ₃]C(CH ₃) ₂ CH ₂ COCH ₃ II I:II = 28:72 (100) I:II = 0:100 (92)	912 912
	DME Et ₂ O	4-CH ₃ OC ₆ H ₄ COC(CH ₃) ₂ [OSi(CH ₃) ₃]CH=C(CH ₃) ₂ I, 4-CH ₃ OC ₆ H ₄ C(CN)[OSi(CH ₃) ₃]C(CH ₃) ₂ CH ₂ COCH ₃ II I:II = 95:5 (95) I:II = 30:70 (91)
DME Et ₂ O	4-NCC ₆ H ₄ COC(CH ₃) ₂ [OSi(CH ₃) ₃]CH=C(CH ₃) ₂ I, 4-NCC ₆ H ₄ C(CN)[OSi(CH ₃) ₃]C(CH ₃) ₂ CH ₂ COCH ₃ II I:II = 0:100 (95) I:II = 0:100 (96)	912 912
	THF, HMPA, -78°	C ₆ H ₅ C[CH(C ₆ H ₅)CH ₂ NO ₂](CN)OCH(OC ₂ H ₅)CH ₃ (55-85)
THF	 C(C ₆ H ₅)(CN)OCH(OC ₂ H ₅)CH ₃ (>95)	908
"	 C(C ₆ H ₅)(CN)OCH(OC ₂ H ₅)CH ₃ (>95)	908

TABLE XVI. 1,2-ADDITION AND 1,4-ADDITION REACTIONS OF ANIONS OF

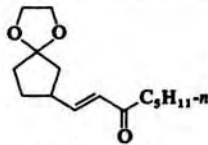
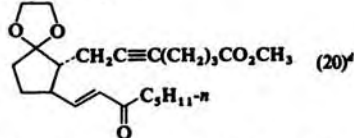
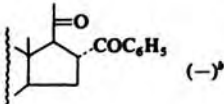
No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₃	$n\text{-C}_3\text{H}_{11}\text{CH}=\text{CHCH}(\text{CN})\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$		LDA
	$4\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{CH}(\text{CN})\text{OSi}(\text{CH}_3)_3$	$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$	"
	$4\text{-CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CN})\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$	"	"
	$n\text{-C}_3\text{H}_{11}\text{CH}=\text{CHCH}(\text{CN})\text{OCH}(\text{OC}_2\text{H}_5)\text{CH}_3$	$\text{C}_6\text{H}_5\text{CH}=\text{CHNO}_2$	"
			NaH
C ₁₄	$2\text{-(CH}_3\text{OCH}_2\text{O)}_2\text{C}_6\text{H}_4\text{CH}(\text{CN})\text{OCH}(\text{OC}_2\text{H}_5)\text{CH}_3$	$\text{C}_6\text{H}_5\text{CH}=\text{CHNO}_2$	LDA

^a The cyanohydrin was generated *in situ* from the corresponding aldehyde.

^b The initial product was hydrolyzed.

^c The initial product was treated with $(\text{CH}_3)_3\text{SiCl}$ and/or bis(trimethylsilyl)acetamide.

PROTECTED CYANOHYDRINS TO VARIOUS MICHAEL ACCEPTORS (*Continued*)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
THF, HMPA, -78°	 (3) ^d	914
	 (20) ^d	
DME Et ₂ O THF, -78°	$4\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{COC}(\text{CH}_3)[\text{OSi}(\text{CH}_3)_3]\text{CH}=\text{C}(\text{CH}_3)_2$ I, $4\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{C}(\text{CN})[\text{OSi}(\text{CH}_3)_3]\text{C}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3$ II I:II = 100:0 (96) I:II = 86:14 (99)	912 912
THF, HMPA, -78°	$4\text{-CH}_3\text{C}_6\text{H}_4\text{C}[\text{COH}(\text{CH}_3)\text{CH}=\text{C}(\text{CH}_3)_2](\text{CN})\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$ (70) $n\text{-C}_3\text{H}_{11}\text{CH}=\text{CHC}[\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{NO}_2](\text{CN})\text{OCH}(\text{OC}_2\text{H}_5)\text{CH}_3$ (55-85)	915 909
DMSO	 (-) ^b	916a
THF, HMPA, -78°	$2\text{-(CH}_3\text{OCH}_2\text{O)}_2\text{C}_6\text{H}_4\text{C}[\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{NO}_2](\text{CN})\text{OCH}(\text{OC}_2\text{H}_5)\text{CH}_3$ (55-85)	909

^d The enolate was trapped with $\text{ICH}_2\text{C}\equiv\text{C}(\text{CH}_2)_3\text{CO}_2\text{CH}_3$, and the initial product was hydrolyzed, converted to its ethylene ketal, and exposed to base.

TABLE XVII. INTRAMOLECULAR REACTIONS OF ANIONS OF PROTECTED CYANOHYDRINS


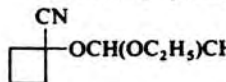
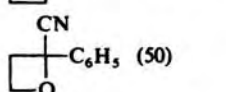
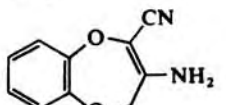

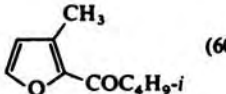
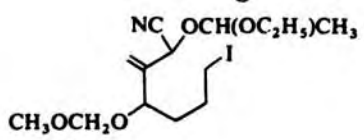
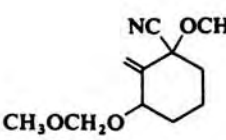
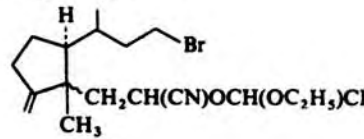
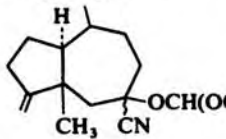
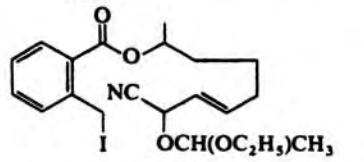
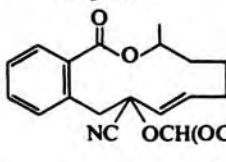
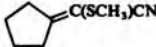
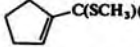
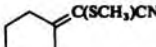
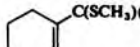
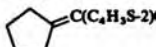
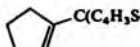
No. of C Atoms	Nucleophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
296 C ₈	Cl(CH ₂) ₂ CH(CN)OCH(OC ₂ H ₅)CH ₃	NaN[Si(CH ₃) ₃] ₂	C ₆ H ₆ , 80°	 (62)	226
C ₉	Cl(CH ₂) ₃ CH(CN)OCH(OC ₂ H ₅)CH ₃	"	"	 (61)	226
C ₁₀	C ₆ H ₅ CH(CN)O(CH ₂) ₂ Cl	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	—	 (50)	194
	1,2-C ₆ H ₄ (OCH ₂ CN) ₂	NaNH ₂	DMSO	 (65)	916b
	"	<i>t</i> -C ₄ H ₉ OK	"	" (62)	916c
C ₁₁	<i>i</i> -C ₄ H ₉ CH(CN)OCH ₂ 	LDA	THF, HMPA, -78°	 (60)	419
C ₁₄		NaN[Si(CH ₃) ₃] ₂	THF, 40°	 (79)	917
C ₁₈		LDA	THF, HMPA, -78°	 (-)	918
297 C ₂₁		NaN[Si(CH ₃) ₃] ₂	THF	 (75)	423

TABLE XVIII. ALKYLATION OF NITRILE-STABILIZED CARBANIONS BEARING α -SULFUR OR α -SELENIUM SUBSTITUENTS

No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃	CH ₃ SCH ₂ CN	C ₆ H ₅ CH ₂ Cl	KOH	DMSO	C ₆ H ₅ CH ₂ CH(CN)SCH ₃ (-)	454
C ₅	(CH ₃) ₂ NCS ₂ CH ₂ CN	CH ₃ I	Aq NaOH, (<i>n</i> -C ₄ H ₉) ₄ NI	-	(CH ₃) ₂ NCS ₂ CH(CH ₃)CN (82)	455,457
		C ₂ H ₅ I	"		(CH ₃) ₂ NCS ₂ CH(C ₂ H ₅)CN (91)	455
		CH ₂ =CHCH ₂ Cl	"		(CH ₃) ₂ NCS ₂ CH(CH ₂ CH=CH ₂)CN (86)	455
		Br(CH ₂) ₆ Br	"		(CH ₃) ₂ NCS ₂ CH(CN)(CH ₂) ₆ Br (56)	455
					[(CH ₃) ₂ NCS ₂ CH(CN)(CH ₂) ₃] ₂ (18)	
C ₆	(CH ₃) ₂ NCS ₂ CH ₂ CN	C ₆ H ₅ CH ₂ Br	"	-	(CH ₃) ₂ NCS ₂ CH(CH ₂ C ₆ H ₅)CN (88)	455
	<i>t</i> -C ₄ H ₉ SCH ₂ CN	<i>n</i> -C ₃ H ₇ Br	LiNH ₂	NH ₃ , THF	<i>t</i> -C ₄ H ₉ SCH(C ₃ H ₇)CN (83)	120
	(CH ₃) ₂ NCS ₂ CH(CH ₃)CN	<i>n</i> -C ₆ H ₁₃ Br	Aq NaOH, (<i>n</i> -C ₄ H ₉) ₄ NI	-	(CH ₃) ₂ NCS ₂ CH(CH ₃)(C ₆ H ₁₃)CN (96)	455,457
		C ₆ H ₅ CH ₂ Br	"		(CH ₃) ₂ NCS ₂ CH(CH ₃)(C ₆ H ₅)CN (91)	455
C ₇	(C ₂ H ₅) ₂ NC(O)SCH ₂ CN	<i>n</i> -C ₃ H ₇ Br	Aq NaOH, (<i>n</i> -C ₄ H ₉) ₄ NI	-	(C ₂ H ₅) ₂ NC(O)SCH(C ₃ H ₇)CN (95)	457
	(CH ₃) ₂ NCS ₂ CH(C ₂ H ₅)CN	<i>n</i> -C ₆ H ₁₃ Br	"		(CH ₃) ₂ NCS ₂ CH(C ₂ H ₅)(C ₆ H ₁₃)CN (88)	455
C ₈	C ₆ H ₅ SCH ₂ CN	CH ₃ I	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	-	C ₆ H ₅ SC(CH ₃) ₂ CN (75)	456
		C ₂ H ₅ Br	"		C ₆ H ₅ SCH(C ₂ H ₅)CN (80)	456
		CH ₂ =CHCH ₂ Br ^a	"		C ₆ H ₅ SC(CH ₂ CH=CH ₂) ₂ CN (80)	456
		Cl(CH ₂) ₂ Cl	"		C ₆ H ₅ SCH(CH ₂) ₂ Cl (39)	456
		CH ₃ I	Aq NaOH, (<i>n</i> -C ₄ H ₉) ₄ NI	-	C ₆ H ₅ SeCH(CH ₃) ₂ CN (96)	458
	C ₆ H ₅ SeCH ₂ CN					
		C ₂ H ₅ I	<i>n</i> -C ₄ H ₉ Li	THF, -78°	 (85)	454
	C ₆ H ₅ SCH ₂ CN	<i>n</i> -C ₄ H ₉ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₂]Cl	-	C ₆ H ₅ SCH(C ₄ H ₉)CN (-)	459
		"	"		" (82)	456
		C ₆ H ₅ CH ₂ Cl	"		C ₆ H ₅ SC(CH ₂ C ₆ H ₅) ₂ CN (82)	456
		"	Aq NaOH, (<i>n</i> -C ₄ H ₉) ₄ NI	-	C ₆ H ₅ SeCH(CH ₂ C ₆ H ₅) ₂ CN (92)	458
		"	"		C ₆ H ₅ SeC(CH ₂ C ₆ H ₅) ₂ CN (70-88)	458
		<i>n</i> -C ₆ H ₁₇ Br ^a	"		C ₆ H ₅ SeCH(C ₆ H ₁₇) ₂ CN (92)	458
		C ₆ H ₅ CH=CHCH ₂ Cl ^a	"		C ₆ H ₅ SeCH(CH ₂ CH=CHC ₆ H ₅) ₂ CN (81)	458
C ₉		C ₂ H ₅ I	<i>n</i> -C ₄ H ₉ Li	THF, -78°	 (82)	454
C ₁₁	4-CH ₃ OC ₆ H ₄ CH ₂ CH(SCH ₃)CN	CH ₃ I	KOH	DMSO	4-CH ₃ OC ₆ H ₄ CH ₂ CH(SCH ₃)(CH ₃)CN (-)	454
	C ₆ H ₅ (CH ₂) ₂ C=C(SCH ₃)CN	C ₂ H ₅ Br	<i>n</i> -C ₄ H ₉ Li	THF, -78°	CH ₂ =C(C ₆ H ₅)(C ₂ H ₅)(SCH ₃)C (59)	454
		X(CH ₂) ₂ Cl ^a			 I	
			NaNH ₂	Toluene	I X = N(CH ₃) ₂ (-)	339
			"	"	I X = N(CH ₃) ₂ (-)	339
C ₁₂	<i>n</i> -C ₃ H ₁₁ CH(SC ₄ H ₉ - <i>t</i>)CN	<i>n</i> -C ₃ H ₇ Br	LiNH ₂	NH ₃ , THF	(<i>n</i> -C ₃ H ₁₁) ₂ C(SC ₄ H ₉ - <i>t</i>)CN (93)	120
C ₁₄	C ₆ H ₅ CH ₂ C(CH ₃)=C(SCH ₃)CN	C ₂ H ₅ I	<i>n</i> -C ₄ H ₉ Li	THF, -78°	C ₆ H ₅ CH=C(CH ₃)(C ₂ H ₅)(SCH ₃)CN (60)	454
	<i>n</i> -C ₆ H ₁₃ CH(SeC ₆ H ₅)CN	CH ₃ I	LDA	"	<i>n</i> -C ₆ H ₁₃ C(SeC ₆ H ₅)(CH ₃)CN (87)	460

^a The precise leaving group in the alkylating agent was unspecified.

TABLE XIX. ARYLATION OF NITRILE-STABILIZED CARBANIONS BEARING α -SULFUR SUBSTITUENTS

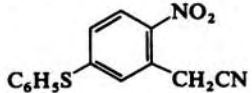
No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃	CH ₃ SCH ₂ CN	1-O ₂ NC ₁₀ H ₇	NaOH	DMSO, 30°	4-O ₂ NC ₁₀ H ₆ CH ₂ CN (75)	279
C ₈	C ₆ H ₅ SCH ₂ CN	C ₆ H ₅ NO ₂	"	"	4-O ₂ NC ₆ H ₄ CH ₂ CN (18), 2-O ₂ NC ₆ H ₄ CH ₂ CN (50)	279
		1-O ₂ NC ₁₀ H ₇	"	"	4-O ₂ NC ₁₀ H ₆ CH ₂ CN (80)	279
		4-O ₂ NC ₆ H ₄ C ₆ H ₅	"	"	2-O ₂ N-5-C ₆ H ₅ C ₆ H ₃ CH ₂ CN (74)	279
		4-(C ₆ H ₅ S)C ₆ H ₄ NO ₂	"	"	 (74)	279

TABLE XX. ADDITION OF NITRILE-STABILIZED CARBANIONS BEARING α -SULFUR SUBSTITUENTS TO ALDEHYDES AND KETONES





No. of C Atoms	Nucleophile	Electrophile	Base	Reactions Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃	CH ₃ SCH ₂ CN		[C ₆ H ₅ CH ₂ N(CH ₃) ₃]OH	THF	 (95)	454
			"	"	 (88)	454
		ArCHO	"	"	ArCH=CH(CN)SCH ₃ I I Ar = C ₆ H ₅ (75) I Ar = 4-CH ₃ OC ₆ H ₄ (74) I Ar = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (85) I Ar = 2-furyl (82) I Ar = N-methyl-3-indolyl (96) I Ar = 2-pyridyl (81)	454
		C ₆ H ₅ COCH ₃	"	"	C ₆ H ₅ C(CH ₃)=C(SCH ₃)CN (30)	454
		C ₆ H ₅ CH ₂ COCH ₃	"	"	C ₆ H ₅ CH ₂ C(CH ₃)=C(SCH ₃)CN (65)	454

TABLE XXI. 1,2-ADDITION AND 1,4-ADDITION OF NITRILE-STABILIZED CARBANIONS BEARING α -SULFUR SUBSTITUENTS TO VARIOUS MICHAEL ACCEPTORS

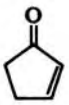
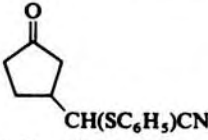
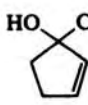

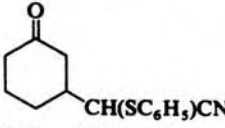
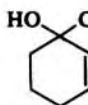
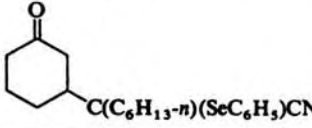
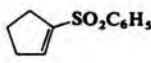
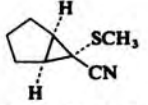
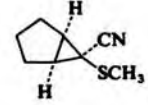
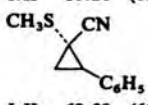
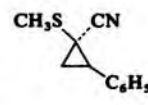
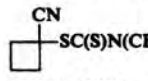


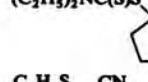
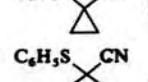


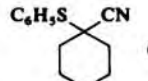


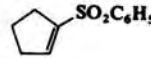
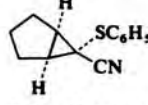
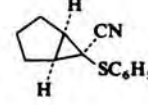
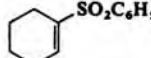
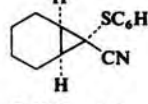
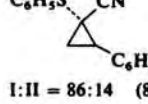
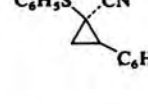
No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.		
C ₈	C ₆ H ₅ SCH ₂ CN		LDA	THF, -78°	 I:II = 89:11 (84)	I,  II 919		
				" THF, 25°	I:II = 100:0 (90)		919	
				" Et ₂ O, -78°	I:II = 86:14 (86)		919	
				" Et ₂ O, 25°	I:II = 98:2 (79)		919	
			"	"	THF, -78°	 I:II = 79:21 (88)	I,  II 919	
					" THF, 25°	I:II = 100:0 (87)		919
					" Et ₂ O, -78°	I:II = 46:54 (83)		919
					" Et ₂ O, 25°	I:II = 100:0 (93)		919
C ₁₄	<i>n</i> -C ₆ H ₁₃ CH(SeC ₆ H ₅)CN	"	"	THF, -78°	 (91)	460		

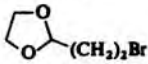
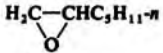
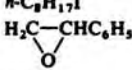

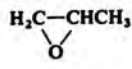

TABLE XXII. INTRAMOLECULAR REACTIONS OF NITRILE-STABILIZED CARBANIONS BEARING α -SULFUR SUBSTITUENTS

No. of C Atoms	Nucleophile	Electrophile	Base	Reactions Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₅	CH ₃ SCH ₂ CN		LDA	THF	 I,  II I:II = 80:20 (61)	391	
		(E)-C ₆ H ₅ CH=CHSO ₂ C ₆ H ₅	"	"	 I,  II I:II = 62:38 (61)	391	
302 C ₅	(CH ₃) ₂ NCS ₂ CH ₂ CN	Br(CH ₂) ₃ Br	Aq NaOH, (n-C ₄ H ₉) ₄ NI	—	 (98)	455	
		Br(CH ₂) ₄ Br	"	—	 (87)	455	
		Br(CH ₂) ₅ Br	"	—	 (~100)	455	
C ₇	(C ₂ H ₅) ₂ NC(S)SCH ₂ CN	Br(CH ₂) ₄ Br	"	—	 (~100)	457	
C ₈	C ₆ H ₅ SCH ₂ CN	Br(CH ₂) ₂ Br	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	—	 (47)	456	
		Br(CH ₂) ₄ Br ^a	"	—	 (69)	456	
C ₈ -C ₁₃	RR'CHSCH(SCH ₃)CN R = CH ₃ , R' = C(CH ₃)=CH ₂ R = H, R' = C(C ₂ H ₅)=CHCH ₃ R = H, R' = CH=CHC ₃ H _{7-n} R = H, R' = 1-Cyclohexenyl R = H, R' = C(C ₆ H ₅)=CH ₂ R = n-C ₃ H ₇ , R' = CH=CHC ₂ H ₅ R = H, R' = 	Br(CH ₂) ₃ Br	"	—	 (50)	456	
		—	LDA	THF	R''C(SCH ₃) ₂ CN I ^b I R'' = CH ₂ C(CH ₃)=CHCH ₃ (70) I R'' = CH(CH ₃)C(C ₂ H ₅)=CH ₂ (86) I R'' = CH(C ₃ H _{7-n})CH=CH ₂ (56) I R'' =  (70) I R'' = CH ₂ C(C ₆ H ₅)=CH ₂ (91) I R'' = CH(C ₆ H ₅)CH=CHC ₃ H _{7-n} (73) I R'' =  (72)	920	
			"	"	"	 I,  II I:II = 82:18 (69)	391
			"	"	"	 (81)	391
		(E)-C ₆ H ₅ CH=CHSO ₂ C ₆ H ₅	"	"	"	 I,  II I:II = 86:14 (83)	391

^a The precise leaving group in the alkylating agent was unspecified.

^b The initial rearrangement product was trapped with CH₃I.

TABLE XXIII. ALKYLATION OF α -(DIALKYLAMINO)NITRILE-STABILIZED

No. of C Atoms	Nucleophile	Electrophile
C ₅	CH ₃ CH(CN)N(CH ₃) ₂	C ₂ H ₅ Br
C ₆	C ₂ H ₅ CH(CN)N(CH ₃) ₂	C ₂ H ₅ Br n-C ₄ H ₉ Br
	(C ₂ H ₅) ₂ NCH ₂ CN	 (Z)-C ₂ H ₅ CH=CH(CH ₂) ₂ I  n-C ₈ H ₁₇ I 
C ₇	(CH ₃) ₂ C=C(CN)N(CH ₃) ₂	CH ₃ I
	 CH(CH ₃)CN	C ₂ H ₅ I
C ₈	CH ₃ CH=C(CN)N(C ₂ H ₅) ₂	CH ₃ I CH ₂ =CHCH ₂ Br 
	 C ₂ H ₅ CHCN	CH ₂ =CHCH ₂ Br
	CH ₃ CH=C(CN)N(C ₂ H ₅) ₂	n-C ₅ H ₁₁ Br C ₆ H ₅ CH ₂ Br
C ₉	(CH ₃) ₂ C=C(CN)N(C ₂ H ₅) ₂	CH ₃ I
	(C ₂ H ₅)CH=C(CN)N(C ₂ H ₅) ₂	"
C ₁₀	C ₆ H ₅ CH(CN)N(CH ₃) ₂	CH ₃ I C ₂ H ₅ Br " " 70% aq NaOH n-C ₄ H ₉ Li C ₂ H ₅ I i-C ₃ H ₇ Br " " CH ₂ =CHCH ₂ Br

CARBANIONS WITH ALKYL HALIDES AND EPOXIDES







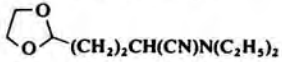
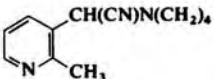


Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
KNH ₂	NH ₃ , Et ₂ O	CH ₃ C(C ₂ H ₅)(CN)N(CH ₃) ₂ (44)	474
"	"	(C ₂ H ₅) ₂ C(CN)N(CH ₃) ₂ (75)	474
"	"	C ₂ H ₅ C(C ₄ H _{9-n})(CN)N(CH ₃) ₂ (70)	474
LDA	THF, HMPA, -78°	 (-)	465
"	"	(Z)-C ₂ H ₅ CH=CH(CH ₂) ₂ CH(CN)N(C ₂ H ₅) ₂ (-)	465
"	"	(E)-n-C ₃ H ₁₁ CH=CHCHO (50) ^a	465
"	"	(C ₂ H ₅) ₂ NCH(C ₈ H _{17-n})CN (90)	465
"	"	(E)-C ₆ H ₅ CH=CHCHO (65) ^a	465
n-C ₄ H ₉ Li	THF, HMPA, -60°	C ₂ H ₅ C(CH ₃)=C(CN)N(CH ₃) ₂ I, CH ₂ =C(CH ₃)C(CH ₃)(CN)N(CH ₃) ₂ II	475
LDA	THF, to -40°	I (54), II (36)	475
"	THF, -78°	I (60), II (28)	475
"	THF, -78°	 (82)	263
"	THF, -30° to -40°	C(CH ₃)(C ₂ H ₅)CN	475
"	THF, -30° to -40°	C ₂ H ₅ CH=C(CN)N(C ₂ H ₅) ₂ (75)	475
"	THF, -30° to -40°	CH ₂ =CH(CH ₂) ₂ CH=C(CN)N(C ₂ H ₅) ₂ (75)	475
n-C ₄ H ₉ Li	THF, HMPA, -60°	CH ₃ CHOHCH ₂ CH ₂ CH=C(CN)N(C ₂ H ₅) ₂ (55)	475
LDA	THF, -78°	 I	263
"	"	C ₂ H ₅ CRCN	475
"	"	I R = CH ₂ CH=CH ₂ (92)	263
"	THF, -30° to -40°	I R = C ₂ H ₅ -n (90)	475
"	THF, -30° to -40°	C ₆ H ₅ (CH ₂) ₂ CH=C(CN)N(C ₂ H ₅) ₂ (65)	475
n-C ₄ H ₉ Li	THF, HMPA, -60°	(C ₂ H ₅)(CH ₃)C=C(CN)N(C ₂ H ₅) ₂ (70)	475
LDA	THF, -30° to -40°	i-C ₃ H ₇ CH=C(CN)N(C ₂ H ₅) ₂ (55)	475
KNH ₂	NH ₃	C ₆ H ₅ C(CH ₃)(CN)N(CH ₃) ₂ (70)	461
LDA	THF, -78°	" (96)	263
KNH ₂	NH ₃	C ₆ H ₅ C(C ₂ H ₅)(CN)N(CH ₃) ₂ (86)	461
"	"	" (92-94)	463
"	"	" (56)	76
"	70% aq NaOH	"	76
n-C ₄ H ₉ Li	Et ₂ O	C ₆ H ₅ COC ₂ H ₅ (42) ^a	463
LDA	THF, -78°	CH ₃ C(C ₂ H ₅)(CN)N(C ₆ H ₅)CH ₃ (89)	263
"	"	C ₆ H ₅ C(C ₂ H ₅)(CN)N(CH ₃) ₂ (62)	76
"	70% aq NaOH	" (88)	461
KNH ₂	NH ₃	" (88)	461
LDA	THF, -78°	" (94)	263
"	"	" (94)	263
"	70% aq NaOH	C ₆ H ₅ C(CH ₂ CH=CH ₂)(CN)N(CH ₃) ₂ (76)	76

TABLE XXIII. ALKYLATION OF α -(DIALKYLAMINO)NITRILE-STABILIZED

No. of C Atoms	Nucleophile	Electrophile
C ₁₀ (Contd.)	C ₆ H ₅ CH(CN)N(CH ₃) ₂	CH ₂ =CHCH ₂ Br
		Br(CH ₂) ₃ Br
		<i>n</i> -C ₄ H ₉ Br ^a
		"
		
		
		C ₆ H ₅ CH ₂ Cl
		"
		4-ClC ₆ H ₄ CH(CN)N(CH ₃) ₂
		C ₆ H ₅ CH(CN)N(CH ₃) ₂
C ₁₁	CH ₃ CH=C(CN)N(CH ₃)C ₆ H ₅ RN(CHO)CH ₂ CN	CH ₃ I
		"
		"
		
		
		4-CH ₃ OC ₆ H ₄ CH(CN)N(CH ₃) ₂
		C ₆ H ₅ CH=CHCH(CN)N(CH ₃) ₂
		"
		RN(CHO)CH ₂ CN
		
C ₁₂	4-ClC ₆ H ₄ CHCN	C ₆ H ₅ CH ₂ Cl
		CH ₃ I
		"
		<i>i</i> -C ₃ H ₇ Br
		CH ₃ I
		"
		"
		C ₆ H ₅ CH ₂ Br
		ClCO ₂ C ₂ H ₅
		
C ₁₀ (Contd.)	C ₆ H ₅ CH(CN)N(CH ₃) ₂	BrCH ₂ CO ₂ C ₂ H ₅
		CH ₂ =CHCH ₂ Cl
		H ₂ C=CHCH ₂ Cl
		

CARBANIONS WITH ALKYL HALIDES AND EPOXIDES (Continued)






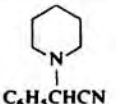
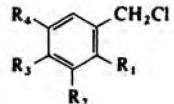
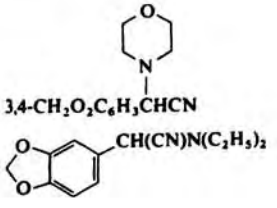
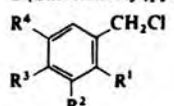
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
LDA	THF, -78°	" (87)	263
"	"	C ₆ H ₅ C[(CH ₂) ₃ Br](CN)N(CH ₃) ₂ (89)	263
70% aq NaOH	—	C ₆ H ₅ C(C ₆ H ₉ - <i>n</i>)(CN)N(CH ₃) ₂ (75)	76
KNH ₂	NH ₃	" (89)	461
LDA	THF, -78°	C ₆ H ₅ C(C ₃ H ₉)(CN)N(CH ₃) ₂ (93)	263
"	"	C ₆ H ₅ C(C ₆ H ₁₁)(CN)N(CH ₃) ₂ (90)	263
70% aq NaOH	"	C ₆ H ₅ C(CH ₂ C ₆ H ₅)(CN)N(CH ₃) ₂ (82)	76
KNH ₂	NH ₃ , Et ₂ O	" (91)	462, 261
"	"	C ₆ H ₅ C(CH ₂ C ₆ H ₄ Cl-4)(CN)N(CH ₃) ₂ (100, crude)	462
"	"	4-ClC ₆ H ₄ C(CH ₂ C ₆ H ₅)(CN)N(CH ₃) ₂ (96)	462
NaNH ₂	"	C ₆ H ₅ C(CN)(N(CH ₃) ₂)CH(CH ₃)C ₆ H ₅ (90)	261
70% aq NaOH	60-70°	(C ₆ H ₅) ₂ C=C(C ₆ H ₅)N(CH ₃) ₂ (-)	76
NaNH ₂	NH ₃ , Et ₂ O	" (79)	261
LDA	THF	C ₂ H ₅ CH=C(CN)N(CH ₃)C ₆ H ₅ (76)	476
NaH	DMF	RN(CHO)CH(CH ₃)CN I	489
"	"	I R = (\pm)-C ₆ H ₅ CH(CH ₃)- (-)	
"	"	I R = S(-)-C ₆ H ₅ CH(CH ₃)- (-)	
"	DMSO, THF, -10°	 C(CH ₃)(CN)N(CH ₂) ₄ (92, crude)	488, 464
LDA	THF, HMPA, -78°	 CO(CH ₂) ₂ CH=CHC ₂ H ₅ (-) ^a	465
KNH ₂	NH ₃ , Et ₂ O	4-CH ₃ OC ₆ H ₄ C(CH ₂ C ₆ H ₅)(CN)N(CH ₃) ₂ (80)	462
LDA	THF	C ₆ H ₅ CH(CH ₃)CH=C(CN)N(CH ₃) ₂ (50), C ₆ H ₅ CH=CHC(CH ₃)(CN)N(CH ₃) ₂ (50)	476
"	"	C ₆ H ₅ CH(C ₃ H ₇ - <i>i</i>)CH=C(CN)N(CH ₃) ₂ (73), C ₆ H ₅ CH=CHC(C ₃ H ₇ - <i>i</i>)(CN)N(CH ₃) ₂ (27)	476
NaH	DMF	RN(CHO)CH(CH ₃)CN I	489
"	"	I R = (S)-(-)-C ₆ H ₅ CH(C ₂ H ₅) (-)	
"	"	I R = (R)-(+)-C ₆ H ₅ CH(C ₂ H ₅) (-)	
"	THF, DMSO	 COR I I R = CH ₃ (78) ^a I R = CH ₂ C ₆ H ₅ (87) ^a	464
"	"	"	464
"	DMF	 I	466
"	"	4-ClC ₆ H ₄ CRCN	
"	"	I R = CO ₂ C ₂ H ₅ (94, crude)	466
"	"	I R = CH ₂ CO ₂ C ₂ H ₅ (34)	466
"	"	I R = CH ₂ CH=CH ₂ (50)	466
"	"	I, R = CH ₂ HC-  CH ₂ (-)	466

TABLE XXIII. ALKYLATION OF α -(DIALKYLAMINO)NITRILE-STABILIZED

No. of C Atoms	Nucleophile	Electrophile
C ₁₃	 C ₆ H ₅ CHCN	CH ₃ I C ₂ H ₅ Br H ₂ C=CHCH ₂ Cl 
C ₁₄	 3,4-CH ₂ O ₂ C ₆ H ₃ CHCN	2-(Chloromethyl)pyridine 
C ₁₅	(C ₆ H ₅) ₂ C=NCH ₂ CN	(CH ₃ O) ₂ SO ₂ C ₂ H ₅ Br <i>i</i> -C ₃ H ₇ Br <i>i</i> -C ₄ H ₉ Br <i>sec</i> -C ₄ H ₉ Br C ₆ H ₅ CH ₂ Cl CH ₃ I C ₂ H ₅ I (<i>E</i>)-CH ₃ CH=CHCH ₂ Cl CH ₃ I <i>i</i> -C ₃ H ₇ CH ₃ I
	C ₆ H ₅ CH(CN)N(C ₆ H ₅)CH ₃	
	C ₆ H ₅ CH=CHCH(CN)N(CH ₂) ₅	
	(<i>S</i>)-(+)-1-C ₁₀ H ₇ CH(CH ₃)N(CHO)CH ₂ CN	

CARBANIONS WITH ALKYL HALIDES AND EPOXIDES (*Continued*)

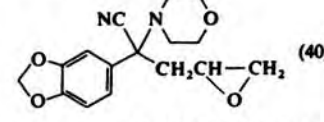
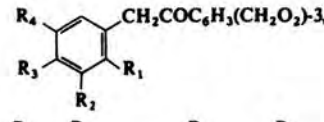
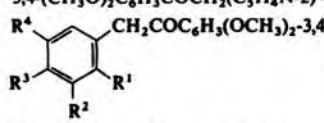
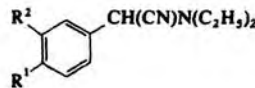
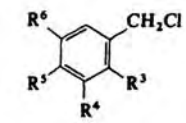
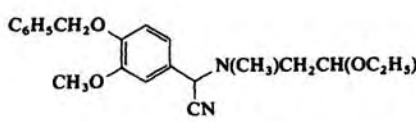
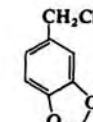
Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																																													
KNH ₂	NH ₃	C ₆ H ₅ C(CH ₃)(CN)N(CH ₂) ₅ (-)	461																																													
"	"	C ₆ H ₅ C(C ₂ H ₅)(CN)N(CH ₂) ₅ (-)	461																																													
NaH	DMF	 (40)	466																																													
"	"	 I ^a	262																																													
		<table border="1"> <thead> <tr> <th>R₁</th> <th>R₂</th> <th>R₃</th> <th>R₄</th> <th>I^a</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>OCH₂C₆H₅</td> <td>OCH₃</td> <td>OCH₃</td> <td>45</td> </tr> <tr> <td>NO₂</td> <td>H</td> <td></td> <td>OCH₂O</td> <td>56</td> </tr> <tr> <td>H</td> <td>OCH₃</td> <td>OCH₃</td> <td>H</td> <td>75</td> </tr> </tbody> </table>	R ₁	R ₂	R ₃	R ₄	I ^a	H	OCH ₂ C ₆ H ₅	OCH ₃	OCH ₃	45	NO ₂	H		OCH ₂ O	56	H	OCH ₃	OCH ₃	H	75																										
R ₁	R ₂	R ₃	R ₄	I ^a																																												
H	OCH ₂ C ₆ H ₅	OCH ₃	OCH ₃	45																																												
NO ₂	H		OCH ₂ O	56																																												
H	OCH ₃	OCH ₃	H	75																																												
"	"	3,4-(CH ₃ O) ₂ C ₆ H ₃ COCH ₂ (C ₂ H ₅ N-2)·HCl (87) ^a	262																																													
"	"	 I ^a	262																																													
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>I^a</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>H</td> <td>H</td> <td>H</td> <td>78</td> </tr> <tr> <td>H</td> <td>H</td> <td>Cl</td> <td>H</td> <td>91</td> </tr> <tr> <td>H</td> <td>H</td> <td>NO₂</td> <td>H</td> <td>83</td> </tr> <tr> <td>H</td> <td>H</td> <td>OCH₃</td> <td>H</td> <td>69</td> </tr> <tr> <td>NO₂</td> <td>H</td> <td>H</td> <td>H</td> <td>75</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>68</td> </tr> <tr> <td>NO₂</td> <td>H</td> <td></td> <td>OCH₂O</td> <td>49</td> </tr> <tr> <td>H</td> <td>OCH₃</td> <td>OCH₃</td> <td>H</td> <td>66</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	I ^a	Cl	H	H	H	78	H	H	Cl	H	91	H	H	NO ₂	H	83	H	H	OCH ₃	H	69	NO ₂	H	H	H	75	H	H	H	H	68	NO ₂	H		OCH ₂ O	49	H	OCH ₃	OCH ₃	H	66	
R ¹	R ²	R ³	R ⁴	I ^a																																												
Cl	H	H	H	78																																												
H	H	Cl	H	91																																												
H	H	NO ₂	H	83																																												
H	H	OCH ₃	H	69																																												
NO ₂	H	H	H	75																																												
H	H	H	H	68																																												
NO ₂	H		OCH ₂ O	49																																												
H	OCH ₃	OCH ₃	H	66																																												
50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl	—	(C ₆ H ₅) ₂ C=NCHRCN I	921																																													
LDA	THF, -78°	I R = CH ₃ (95)																																														
"	"	I R = C ₂ H ₅ (90)																																														
"	"	I R = C ₃ H ₇ - <i>i</i> (79)																																														
"	"	I R = C ₄ H ₉ - <i>i</i> (76)																																														
"	"	I R = C ₄ H ₉ - <i>sec</i> (82)																																														
"	"	I R = CH ₂ C ₆ H ₅ (75)																																														
"	"	C ₆ H ₅ C(CH ₃)(CN)N(C ₆ H ₅)CH ₃ (83)	263																																													
"	"	C ₆ H ₅ C(C ₂ H ₅)(CN)N(C ₆ H ₅)CH ₃ (90)	263																																													
"	"	C ₆ H ₅ C(CH ₂ CH=CHCH ₃)(CN)N(C ₆ H ₅)CH ₃ (87)	263																																													
"	THF	C ₆ H ₅ CH(CH ₃)CH=C(CN)N(CH ₂) ₅ (44),	476																																													
"	"	C ₆ H ₅ CH=CHC(CH ₃)(CN)N(CH ₂) ₅ (56)																																														
"	"	C ₆ H ₅ CH(C ₃ H ₇ - <i>i</i>)CH=C(CN)N(CH ₂) ₅ (63),	476																																													
"	"	C ₆ H ₅ CH=CHC(C ₃ H ₇ - <i>i</i>)(CN)N(CH ₂) ₅ (37)																																														
NaH	DMF	(<i>S</i>)-(+)-1-C ₁₀ H ₇ CH(CH ₃)N(CHO)CH(CH ₃)CN (-)	489																																													

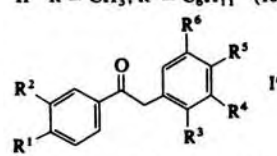
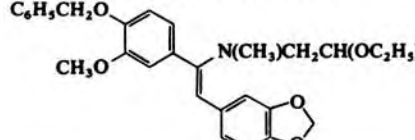
TABLE XXIII. ALKYLATION OF α -(DIALKYLAMINO)NITRILE-STABILIZED

No. of C Atoms	Nucleophile	Electrophile
C ₁₆	<i>t</i> -C ₄ H ₉ CO(CH ₂) ₂ CH(CN)N(C ₆ H ₅)CH ₃ or <i>t</i> -C ₄ H ₉ C[OSi(CH ₃) ₃]=CHCH ₂ CH(CN)N(C ₆ H ₅)CH ₃	CH ₃ I 1. CH ₃ I 2. C ₆ H ₅ CH ₂ Br
C ₁₇	C ₆ H ₅ CH=CHCH(CN)NRR'	CH ₃ I <i>i</i> -C ₃ H ₇ Br
C ₂₀		
		

* The initial product was hydrolyzed.

^b The precise leaving group in the alkylating agent was unspecified.

CARBANIONS WITH ALKYL HALIDES AND EPOXIDES (Continued)

Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																												
LDA	THF	<i>t</i> -C ₄ H ₉ COCH ₂ CH ₂ COCH ₃ (74) ^a	922																												
"	"	<i>t</i> -C ₄ H ₉ COCH(CH ₂ C ₆ H ₅)CH ₂ COCH ₃ (60) ^a	922																												
"	"	C ₆ H ₅ CH(CH ₃)CH=C(CN)NRR' I I R = CH ₃ , R' = C ₆ H ₅ (100) I R = CH ₃ , R' = C ₆ H ₁₁ (100)	476																												
"	"	C ₆ H ₅ CH(C ₂ H ₅)CH=C(CN)NRR' II II R = CH ₃ , R' = C ₆ H ₅ (100) II R = CH ₃ , R' = C ₆ H ₁₁ (100)	476																												
NaH	DMF	 I ^a	262																												
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>R⁵</th> <th>R⁶</th> <th>I^a</th> </tr> </thead> <tbody> <tr> <td>OCH₂C₆H₅</td> <td>OCH₃</td> <td>H</td> <td>O—CH₂—O</td> <td>H</td> <td>H</td> <td>61</td> </tr> <tr> <td>OCH₃</td> <td>OCH₂C₆H₅</td> <td>H</td> <td>O—CH₂—O</td> <td>H</td> <td>H</td> <td>74</td> </tr> <tr> <td>OCH₃</td> <td>OCH₂C₆H₅</td> <td>H</td> <td>OCH₃</td> <td>OCH₃</td> <td>OCH₃</td> <td>63</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	I ^a	OCH ₂ C ₆ H ₅	OCH ₃	H	O—CH ₂ —O	H	H	61	OCH ₃	OCH ₂ C ₆ H ₅	H	O—CH ₂ —O	H	H	74	OCH ₃	OCH ₂ C ₆ H ₅	H	OCH ₃	OCH ₃	OCH ₃	63	
R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	I ^a																									
OCH ₂ C ₆ H ₅	OCH ₃	H	O—CH ₂ —O	H	H	61																									
OCH ₃	OCH ₂ C ₆ H ₅	H	O—CH ₂ —O	H	H	74																									
OCH ₃	OCH ₂ C ₆ H ₅	H	OCH ₃	OCH ₃	OCH ₃	63																									
"	"	 (-)	923																												

^a This material was generated *in situ* by using a Sommelet-Hauser rearrangement of the quaternary salt I;

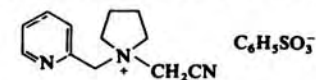



TABLE XXIV. TANDEM CONJUGATE ADDITION-ALKYLATION OF α -(DIALKYLAMINO)ACRYLONITRILES WITH ALKYL HALIDES

No. of C Atoms	Acceptor	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀	CH ₂ =C(CN)N(C ₆ H ₅)CH ₃	<i>t</i> -C ₄ H ₉ Li	CH ₃ I	LDA	THF, -78°	<i>t</i> -C ₄ H ₉ CH ₂ COCH ₃ (80) ^a	126
		"	C ₆ H ₅ CH ₂ Br	"	"	<i>t</i> -C ₄ H ₉ CH ₂ COCH ₂ C ₆ H ₅ (92) ^a	126
		C ₆ H ₅ Li	C ₂ H ₅ I	"	"	C ₆ H ₅ CH ₂ COC ₂ H ₅ (70) ^a	126
		"	C ₆ H ₅ CH ₂ Br	"	"	(C ₆ H ₅ CH ₂) ₂ CO (66) ^a	126
		C ₆ H ₅ CH=CHCH(C ₆ H ₅)Li	C ₆ H ₅ CH ₂ Br	"	"	C ₆ H ₅ CH=CHCH(C ₆ H ₅)CH ₂ COCH ₂ C ₆ H ₅ (65) ^a	126
		C ₆ H ₅ C[N(C ₆ H ₅)CH ₃]=CHCH ₂ Li	CH ₃ I	"	"	C ₆ H ₅ CO(CH ₂) ₃ COCH ₃ (74) ^a	126
		"	C ₆ H ₅ CH ₂ Br	"	"	C ₆ H ₅ CO(CH ₂) ₃ COCH ₂ C ₆ H ₅ (66) ^a	126


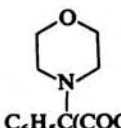
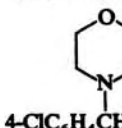
^a The initial product was hydrolyzed.

TABLE XXV. ARYLATION OF α -(DIALKYLAMINO)NITRILE-STABILIZED CARBANIONS

No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂		4-O ₂ NC ₆ H ₄ F	NaH	DMF	4-O ₂ NC ₆ H ₄ COC ₆ H ₅ (89) ^a	466
		4-NCC ₆ H ₄ F	"	"	4-NCC ₆ H ₄ COC ₆ H ₅ (88) ^a	466
		2,4-(O ₂ N)CF ₃ C ₆ H ₃ Cl	"	"	2,4-(O ₂ N)CF ₃ C ₆ H ₃ COC ₆ H ₅ (92) ^a	466

^a The initial product was hydrolyzed.

TABLE XXVI. ACYLATION OF α -(DIALKYLAMINO)NITRILE-STABILIZED CARBANIONS

No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂	 C ₆ H ₅ CHCN	4-ClC ₆ H ₄ COCl	NaH	DMF	 C ₆ H ₅ C(COC ₆ H ₄ Cl-4)CN	(50) 466
	 4-ClC ₆ H ₄ CHCN	"	"	"	(4-ClC ₆ H ₄ CO) ₂	(31-36)* 466

* The initial product was hydrolyzed.

TABLE XXVII. ADDITION OF α -(DIALKYLAMINO)NITRILE-STABILIZED CARBANIONS TO ALDEHYDES AND KETONES


















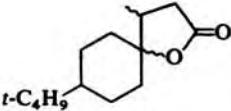
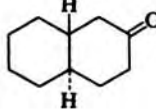
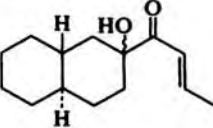
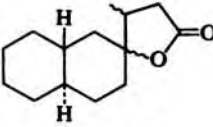
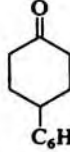
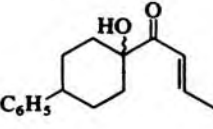
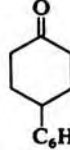
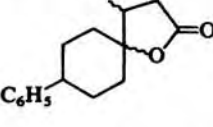

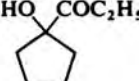

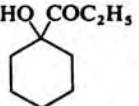
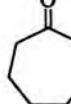
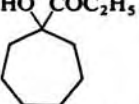
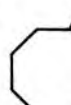
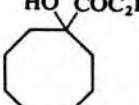
No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃	CH ₂ =NCH ₂ CN	ArCHO	1. NaOC ₂ H ₅ 2. CH ₃ CO ₂ H	C ₂ H ₅ OH	ArCH=CHCN I	467
		"	NaOC ₂ H ₅	"	ArCH=C(CN)N=CHAr II	479
					I Ar = C ₆ H ₅ (-) I Ar = 4,3-C ₂ H ₅ O(CH ₃ O)C ₆ H ₃ (-) I Ar = 2,4-(C ₂ H ₅ O) ₂ C ₆ H ₃ (-) I Ar = 2,4-C ₂ H ₅ O(CH ₃ O)C ₆ H ₃ (-) I Ar = 4,2-C ₂ H ₅ O(CH ₃ O)C ₆ H ₃ (-) II Ar = 4-CH ₃ OC ₆ H ₄ (-) II Ar = 4-C ₂ H ₅ OC ₆ H ₄ (-) II Ar = 4-C ₆ H ₅ CH ₂ OC ₆ H ₄ (-) II Ar = 4-(CH ₃) ₂ NC ₆ H ₄ (-) II Ar = 3,4-CH ₂ O ₂ C ₆ H ₃ (-) II Ar = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (-) II Ar = 2,4-(CH ₃ O) ₂ C ₆ H ₃ (-)	
C ₇	CH ₃ CH(CN)N(C ₂ H ₅) ₂		LDA	THF, -78°	 (55) ^a	468
		<i>n</i> -C ₅ H ₁₁ CHO	"	"	<i>n</i> -C ₅ H ₁₁ CHOHCOCH ₃ (69) ^a	468
			"	"	 (68) ^a	468
	CH ₃ CH=CHCN(CN)N(CH ₃) ₂	"	LDA, ZnCl ₂	"	 (45) ^a	477
			"	THF, 0°	 (78) ^a	477
CH ₃ CH(CN)N(C ₂ H ₅) ₂	<i>n</i> -C ₆ H ₁₃ CHO	LDA	THF, -78°	<i>n</i> -C ₆ H ₁₃ CHOHCOCH ₃ (73) ^a	468	
		"	"	 (74) ^a	468	
	<i>n</i> -C ₇ H ₁₅ CHO	"	"	<i>n</i> -C ₇ H ₁₅ CHOHCOCH ₃ (70) ^a	468	
		"	"	 (76) ^a	468	
CH ₃ CH=CHCH(CN)N(CH ₃) ₂		LDA, ZnCl ₂	THF, 0°	 (63) ^a	477	
		LDA	"	 (53) ^a	477	
		LDA, ZnCl ₂	THF, -78°	 (61) ^a	477	
	C ₄ H ₉ - <i>t</i>					

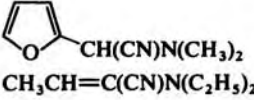
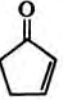
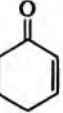
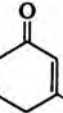
TABLE XXVII. ADDITION OF α -(DIALKYLAMINO)NITRILE-STABILIZED CARBANIONS TO ALDEHYDES AND KETONES (Continued)

No. of C Atoms	Nucleophile	Electrophile	Base	Reactions Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇ (Contd.)	CH ₃ CH=CHCH(CN)N(CH ₃) ₂		LDA	THF, 0°	 (43) ^a	477
			LDA, ZnCl ₂	THF, -78°	 (26) ^a	477
		"	"	THF, 0°	 (71) ^a	477
			"	THF, -78°	 (46) ^a	477
			"	THF, 0°	 (51) ^a	477
		<i>n</i> -C ₁₃ H ₂₇ CHO	LDA	THF, -78°	<i>n</i> -C ₁₃ H ₂₇ CHOHCOCH ₃ (72) ^a	468
C ₈	C ₂ H ₅ CH(CN)N(C ₂ H ₅) ₂		"	"	 (60) ^a	468
		<i>n</i> -C ₅ H ₁₁ CHO	"	"	<i>n</i> -C ₅ H ₁₁ CH(OH)COC ₂ H ₅ (62) ^a	468
			"	"	 (72) ^a	468
		<i>n</i> -C ₆ H ₁₃ CHO	"	"	<i>n</i> -C ₆ H ₁₃ CHOHCOC ₂ H ₅ (68) ^a	468
			"	"	 (73) ^a	468
		<i>n</i> -C ₇ H ₁₅ CHO	"	"	<i>n</i> -C ₇ H ₁₅ CHOHCOC ₂ H ₅ (67) ^a	468
			"	"	 (78) ^a	468
C ₁₁	CH ₃ CH=C(CN)N(CH ₃)C ₆ H ₅	<i>n</i> -C ₁₃ H ₂₇ CHO	"	"	<i>n</i> -C ₁₃ H ₂₇ CHOHCOC ₂ H ₅ (57) ^a	468
		CH ₃ COCH ₃	"	THF	(CH ₃) ₂ COHCH ₂ CH=C(CN)N(CH ₃)C ₆ H ₅ (63)	476
		C ₆ H ₅ CHO	"	"	C ₆ H ₅ CHOHCH ₂ CH=C(CN)N(CH ₃)C ₆ H ₅ (81)	476
		(C ₆ H ₅) ₂ CO	"	"	(C ₆ H ₅) ₂ C[OSi(CH ₃) ₃]CH ₂ CH=C(CN)N(CH ₃)C ₆ H ₅ (80) ^b	476
C ₁₂	(CH ₃) ₃ SiCH(CN)N(C ₆ H ₅)CH ₃	HCHO	"	"	CH ₂ =C(CN)N(C ₆ H ₅)CH ₃ (83)	126

^a The initial product was hydrolyzed.

^b The initial product was treated with (CH₃)₃SiCl.

TABLE XXVIII. 1,2-ADDITION AND 1,4-ADDITION OF α -(DIALKYLAMINO)NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₈	 <chem>Cc1ccoc1CNC(C)C</chem>	CH ₂ =CHCN	NaOCH ₃
		CH ₂ =CHCOCH ₃	LDA
			"
			"
		(CH ₃) ₂ C=CHCOCH ₃	"
			"
	Isophorone	"	"
	Carvone	"	"
C ₁₀	<chem>Cc1ccc(CNC(C)C)cc1</chem> <chem>Cc1ccc(CNC(C)C)cc1</chem>	CH ₂ =CHCN	NaOCH ₃

STABILIZED CARBANIONS TO VARIOUS MICHAEL ACCEPTORS



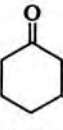
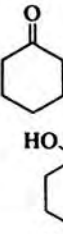
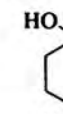
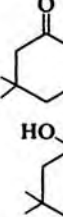
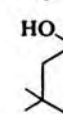
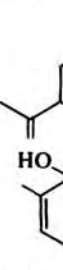
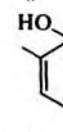
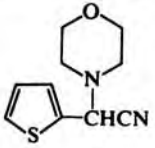
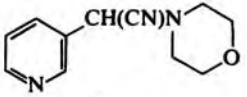
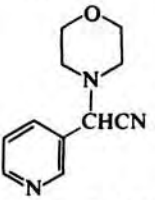
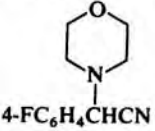




Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
DME	 (72) ^a	473
THF, -60°	CH ₃ CO(CH ₂) ₃ CH=C(CN)N(C ₂ H ₅) ₂ (60)	475
THF, -50°	 (65)	475
"	 (65)	475
THF, -60°	(CH ₃) ₂ C=CHC(OH)(CH ₃)CH ₂ CH=C(CN)N(C ₂ H ₅) ₂ (38), CH ₃ COCH ₂ C(CH ₃) ₂ CH ₂ CH=C(CN)N(C ₂ H ₅) ₂ (33)	475
THF, -60° to -20°	 (36),  (32)	475
THF, -60°	 (16-38),  (10-40)	475
"	 (45-65),  (20-30)	475
DME	C ₆ H ₅ CO(CH ₂) ₂ CN (71) ^a	473
"	4-ClC ₆ H ₄ CO(CH ₂) ₂ CN (75) ^a	473

TABLE XXVIII. 1,2-ADDITION AND 1,4-ADDITION OF α -(DIALKYLAMINO)NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₀ (Contd.)		CH ₂ =CHCO ₂ C ₂ H ₅	KOH
C ₁₁		"	"
		CH ₂ =CHCOC ₆ H ₅	"
C ₁₂	3,4-(CH ₃ O) ₂ C ₆ H ₃ CH(CN)N(CH ₃) ₂ (Z)-C ₂ H ₅ CH=CH(CH ₂) ₂ CH(CN)N(C ₂ H ₅) ₂	CH ₂ =CHCN CH ₂ =CHCOCH ₃	NaOCH ₃ LDA
		CH ₂ =C(CH ₃)CN	KOH
		CH ₃ CH=CHCN	"
		CH ₂ =CHCO ₂ C ₂ H ₅	"
		C ₆ H ₅ CH=CHCN	"
C ₁₃		CH ₂ =C(CH ₃)CN CH ₃ CH=CHCN C ₆ H ₅ CH=CHCN CH ₂ =CHCO ₂ C ₂ H ₅ " "	"

STABILIZED CARBANIONS TO VARIOUS MICHAEL ACCEPTORS (Continued)

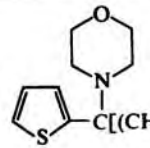
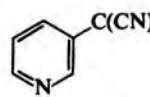
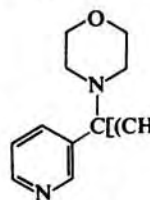
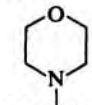
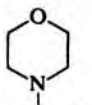
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂ H ₅ OH, THF	 (97)	470
CH ₃ OH, <i>t</i> -C ₄ H ₉ OH	 (90)	471
CH ₃ OH, C ₂ H ₅ OH, Et ₂ O	 (-)	469
DME	3,4-(CH ₃ O) ₂ C ₆ H ₃ CO(CH ₂) ₂ CN (70) ^a	473
THF, HMPA, -78°	(Z)-C ₂ H ₅ CH=CH(CH ₂) ₂ CO(CH ₂) ₂ COCH ₃ (72) ^a	465
C ₂ H ₅ OH, THF	 I 4-FC ₆ H ₄ CRCN I R = CH ₂ CH(CH ₃)CN (40) I R = CH(CH ₃)CH ₂ CN (89)	470
"	"	470
"	 II XC ₆ H ₄ CRCN II X = F-2, R = (CH ₂) ₂ CO ₂ C ₂ H ₅ (81) II X = Cl-2, R = (CH ₂) ₂ CO ₂ C ₂ H ₅ (98) II X = F-3, R = (CH ₂) ₂ CO ₂ C ₂ H ₅ (44) II X = Cl-4, R = CH(C ₆ H ₅)CH ₂ CN (-)	470
"	"	470
"	II X = CF ₃ -3, R = CH ₂ CH(CH ₃)CN (64) II X = CF ₃ -3, R = CH(CH ₃)CH ₂ CN (55) II X = CF ₃ -3, R = CH(C ₆ H ₅)CH ₂ CN (-) II X = CF ₃ -3, R = (CH ₂) ₂ CO ₂ C ₂ H ₅ (81) II X = CF ₃ -4, R = (CH ₂) ₂ CO ₂ C ₂ H ₅ (57) II X = CH ₃ -3, R = (CH ₂) ₂ CO ₂ C ₂ H ₅ (99)	470

TABLE XXVIII. 1,2-ADDITION AND 1,4-ADDITION OF α -(DIALKYLAMINO)NITRILE-

No. of C Atoms	Nucleophile	Electrophile	Base
C ₁₅		CH ₂ =CHCO ₂ C ₂ H ₅	KOH
C ₁₆		"	"
C ₁₇		[1- ¹⁴ C, ¹³ C]CH ₂ =CHCN	"

* The initial product was hydrolyzed.

STABILIZED CARBANIONS TO VARIOUS MICHAEL ACCEPTORS (*Continued*)

Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂ H ₅ OH, THF	(49)	470
"	(94)	470
<i>t</i> -C ₄ H ₉ OH, CH ₃ OH	(-)	472

TABLE XXIX. INTRAMOLECULAR REACTIONS OF α -(DIALKYLAMINO)NITRILE-STABILIZED CARBANIONS OR TETRAALKYLAMMONIUM YLIDS

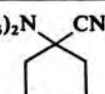
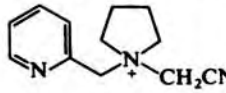
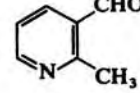
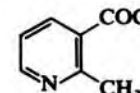
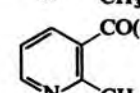
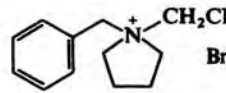
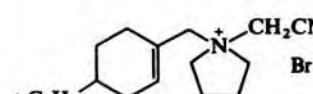
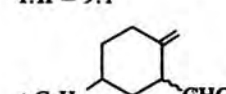
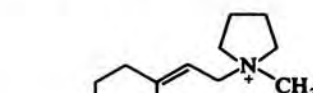
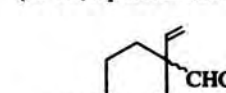
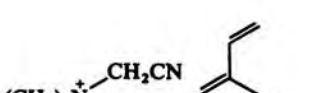

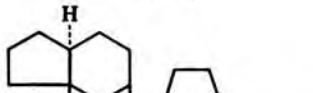
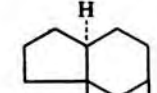
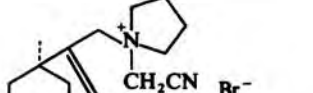
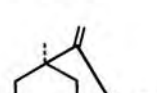
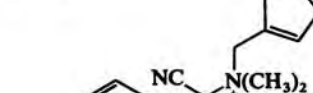

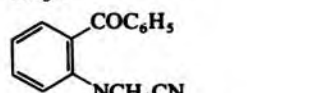
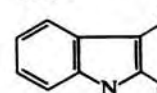
No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆	(C ₂ H ₅) ₂ NCH ₂ CN	Cl(CH ₂) ₂ Cl	LDA	THF, HMPA, -78°	 (73)	465
C ₁₁	[(CH ₃) ₂ C=CHCH ₂ N(C ₂ H ₅) ₂ CH ₂ CN]Cl	—	KOH	—	CH ₂ =CHC(CH ₃) ₂ CHO (-)	480
C ₁₂	 C ₆ H ₅ SO ₃ ⁻	—	<i>t</i> -C ₄ H ₉ OK	THF, DMSO, -10°	 (50) ^a	464
		—	NaH	"	 (53) ^a	488,464
		—	"	"	 (-) ^a	488
C ₁₃	 Br ⁻	—	<i>t</i> -C ₄ H ₉ OK	THF, DMSO	2-CH ₃ C ₆ H ₄ CHO I, C ₆ H ₅ CH ₂ CHO II I:II = 9:1	481
C ₁₇	 Br ⁻	—	"	"	 <i>t</i> -C ₄ H ₉ (90-95; equatorial:axial CHO = 2:3) ^a	481
C ₁₈	 Br ⁻	—	"	"	 <i>t</i> -C ₄ H ₉ (90-95; equatorial:axial CHO = 9:1) ^a	481
	 Br ⁻	—	"	THF, -30°	(CH ₃) ₂ NCH(CN)  (-)	483
	 Br ⁻	—	"	THF, DMSO	 (-)	486
C ₁₉	 Br ⁻	—	"	"	 (90-95) ^a	481,482
	 Cl ⁻	—	"	DMSO, THF, -30°	 (46) ^a	484
C ₂₂		—	"	<i>t</i> -C ₄ H ₉ OH	 (31) ^b	924

TABLE XXIX. INTRAMOLECULAR REACTIONS OF α -(DIALKYLAMINO)NITRILE-STABILIZED CARBANIONS OR TETRAALKYLAMMONIUM YLIDS (Continued)

No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₂₃		Br ⁻	-	<i>t</i> -C ₄ H ₉ OK	DMSO, THF, -10°	(100)	485
C ₂₆		Br ⁻	-	"	THF, <i>t</i> -C ₄ H ₉ OH	(-)	925
C ₃₀		-	-	"	THF, DMSO, H ₂ O	(-) ^a	487

^a The initial product was hydrolyzed.

^b The initial product was dehydrated by using thionyl chloride in pyridine.

^c The product was the result of rearrangement, alkylation with Br(CH₂)₂CN, and hydrolysis.

^d The product was the result of rearrangement, alkylation with Br(CH₂)₃CN, and hydrolysis.

TABLE XXX. ALKYLATION OF α -HALONITRILE-STABILIZED CARBANIONS








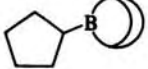
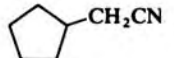
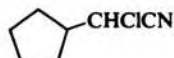


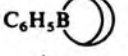
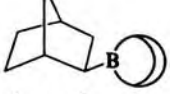

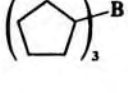
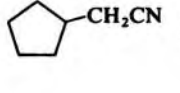
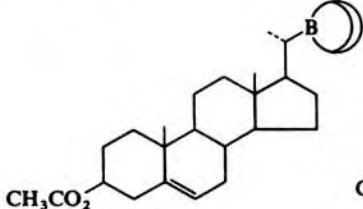
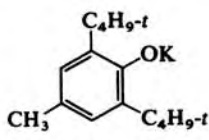
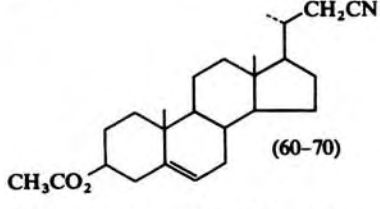
No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₂	ClCH ₂ CN Cl ₂ CHCN	(C ₂ H ₅) ₃ B	KDTBP	—	<i>n</i> -C ₃ H ₇ CN (95)	317	
		"	"	—	C ₂ H ₅ CHClCN (89)	319	
	ClCH ₂ CN	C ₂ H ₅ B 	"	"	—	" (87)	319
		(<i>n</i> -C ₄ H ₉) ₃ B	"	"	—	<i>n</i> -C ₅ H ₁₁ CN (89)	317
		<i>n</i> -C ₄ H ₉ B 	"	"	—	" (76)	317
		<i>sec</i> -C ₄ H ₉ B 	"	"	—	<i>sec</i> -C ₄ H ₉ CH ₂ CN (65)	317
		<i>i</i> -C ₄ H ₉ B 	"	"	—	<i>i</i> -C ₄ H ₉ CH ₂ CN (57)	317
	Cl ₂ CHCN	<i>n</i> -C ₄ H ₉ B 	"	"	—	<i>n</i> -C ₄ H ₉ CHClCN (75)	319
		<i>i</i> -C ₄ H ₉ B 	"	"	—	<i>i</i> -C ₄ H ₉ CHClCN (73)	319
		<i>sec</i> -C ₄ H ₉ B 	"	"	—	<i>sec</i> -C ₄ H ₉ CHClCN (69)	319
	ClCH ₂ CN		"	"	—	 (72)	317
	Cl ₂ CHCN	"	"	"	—	 (76)	319

TABLE XXX. ALKYLATION OF α -HALONITRILE-STABILIZED CARBANIONS (Continued)

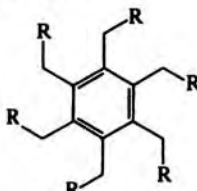
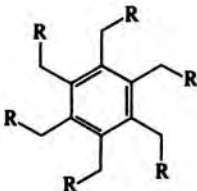
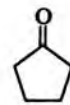
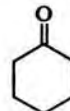
No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂ (Contd.)	ClCH ₂ CN		KDTBP	—	C ₆ H ₁₁ CH ₂ CN (77)	317
	Cl ₂ CHCN		"	—	C ₆ H ₁₁ CHClCN (78)	319
	ClCH ₂ CN		"	—	C ₆ H ₅ CH ₂ CN (75)	317
			"	—	 -CH ₂ CN (65)	317
			"	—	 -CH ₂ CN (67)	317
C ₈				THF, 0°	 (60-70)	926
	C ₆ H ₅ CHClCN*	C ₆ H ₅ CHClCN*	50% NaOH, CCl ₄	—	(E)-C ₆ H ₅ (CN)=C(CN)C ₆ H ₅ (37)	79
	C ₆ H ₅ CHBrCN	C ₆ H ₅ CHBrCN	[C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl Guanidine carbonate	—	" (—)	496

* The α -chloronitrile was generated *in situ* from the corresponding nitrile.

TABLE XXXI. ARYLATION OF α -HALONITRILE-STABILIZED CARBANIONS

No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂	ClCH ₂ CN	4-ClC ₆ H ₄ NO ₂	NaOH	DMSO, 30°	2,5-O ₂ N(Cl)C ₆ H ₃ CH ₂ CN (40)	279
		1-O ₂ NC ₁₀ H ₇	"	"	1-O ₂ NC ₁₀ H ₆ [CH ₂ CN]-2 (75)	279

TABLE XXXII. DARZENS GLYCIDONITRILE SYNTHESIS: REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile	Base
C ₂	ClCH ₂ CN	CH ₃ COCH ₃	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
	"	"	50% aq NaOH, 
	"	"	R = S(CH ₂) ₂ O(CH ₂) ₂ O(CH ₂) ₂ OCH ₃ , NaOC ₂ H ₅
	C ₂ H ₅ COCH ₃	"	"
	<i>n</i> -C ₄ H ₉ CHO	"	<i>t</i> -C ₅ H ₁₁ ONa
	<i>n</i> -C ₃ H ₇ COCH ₃	"	"
	C ₂ H ₅ COC ₂ H ₅	"	50% aq NaOH, 
	"	"	R = S(CH ₂) ₂ O(CH ₂) ₂ O(CH ₂) ₂ OCH ₃ , NaOC ₂ H ₅
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
	"	"	<i>t</i> -C ₄ H ₉ OK NaOC ₂ H ₅
	<i>i</i> -C ₄ H ₉ COCH ₃	"	<i>t</i> -C ₄ H ₉ OK
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl

α-HALONITRILE-STABILIZED CARBANIONS WITH ALDEHYDES AND KETONES

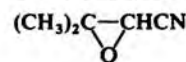
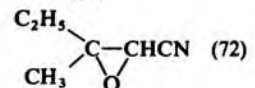
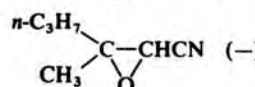
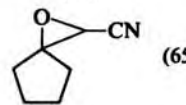
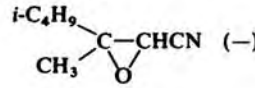
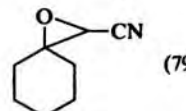

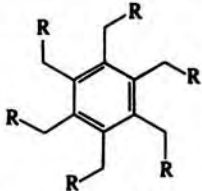
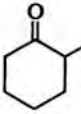
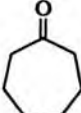
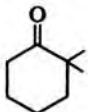
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	 (60)	526
—	" (59)	530
Et ₂ O, -10°	" (67)	513
"	 (72)	513
Xylene, -10°	<i>n</i> -C ₄ H ₉ CH-CHCN (-)	522,523
"	 (-)	522,523
—	(C ₂ H ₅) ₂ C-CHCN (28-45)	530
Et ₂ O, -10°	" (53)	514
—	 (65)	526
<i>t</i> -C ₄ H ₉ OH	" (74)	518
Et ₂ O, -10°	" (73)	513
Et ₂ O, 0°	<i>i</i> -C ₄ H ₉ -C-CHCN (-) 	520
—	 (79)	526

TABLE XXXII. DARZENS GLYCIDONITRILE SYNTHESIS: REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile	Base
C ₂ (Contd.)	ClCH ₂ CN		50% aq NaOH, 
		"	R = S(CH ₂) ₂ O(CH ₂) O(CH ₂) ₂ OCH ₃
		"	<i>t</i> -C ₅ H ₁₁ ONa
		"	<i>t</i> -C ₄ H ₉ OK
		"	NaOC ₂ H ₅
			50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
			<i>t</i> -C ₄ H ₉ OK
		C ₆ H ₅ CHO	NaH
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
		"	50% aq NaOH, dibenzo[18]crown-6
		"	NaOCH ₃
		"	NaOC ₂ H ₅
"	<i>t</i> -C ₄ H ₉ ONa		
"	NaOC ₂ H ₅		
4-CH ₃ OC ₆ H ₄ CHO	"		
"	"		
4-CH ₃ C ₆ H ₄ CHO	"		
<i>n</i> -C ₆ H ₁₃ COCH ₃	<i>t</i> -C ₄ H ₉ OK		
6-Methyl-5-hepten-2-one	"		
	"		

 α -HALONITRILE-STABILIZED CARBANIONS WITH ALDEHYDES AND KETONES (Continued)

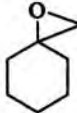
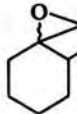
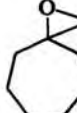
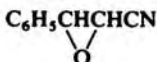


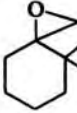
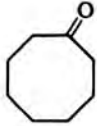
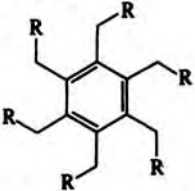
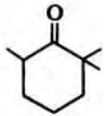
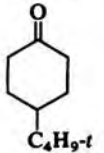
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	 (32-76)	530
Xylene, -10°	" (89)	523
<i>t</i> -C ₄ H ₉ OH	" (79)	518
Et ₂ O, -10°	" (-)	513,927
—	 (78)	526
Et ₂ O, 0°	 (-)	520
Various solvents	C ₆ H ₅ CHCHCN 	E:Z = 50-62:38-50
—	" (75)	505 526
Et ₂ O	" (78)	527
Et ₂ O, -10°	" (40)	509,510
<i>t</i> -C ₄ H ₉ OH	" (-)	515,927
Et ₂ O, -25°	" (49)	518
Et ₂ O, -10°	C ₆ H ₅ CHOHCHClCN (43) 4-CH ₃ OC ₆ H ₄ CH—CHCN (31)	516 515
Et ₂ O, -25°	4-CH ₃ OC ₆ H ₄ CHOHCH(Cl)CN (28) 4-CH ₃ C ₆ H ₄ CHOHCH(Cl)CN (20)	502 502
Et ₂ O, 0°	<i>n</i> -C ₆ H ₁₃ C—CHCN (-) CH ₃ 	520
"	(CH ₃) ₂ C=CH(CH ₂) ₂ C—CHCN (-) CH ₃ 	520
<i>t</i> -C ₄ H ₉ OH	 (64)	518

TABLE XXXII. DARZENS GLYCIDONITRILE SYNTHESIS: REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile	Base
C ₂ (Contd.)	ClCH ₂ CN		<i>t</i> -C ₄ H ₉ OK
		C ₆ H ₅ COCH ₃	NaH 50% aq NaOH, [(C ₆ H ₁₃) ₃ NC ₂ H ₅]Br or [(C ₂ H ₅) ₃ NC ₆ H ₅]Br or [(<i>n</i> -C ₄ H ₉) ₃ NCH ₂ C ₆ H ₅]Br
		"	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl
		"	50% aq NaOH, 
		"	R = S(CH ₂) ₂ O(CH ₂) ₂ O(CH ₂) ₂ OCH ₃
		"	NaOCH ₃
		"	NaOC ₂ H ₅
		"	<i>t</i> -C ₄ H ₉ OK
		"	<i>t</i> -C ₄ H ₉ ONa
		"	NaNH ₂
		3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO	<i>t</i> -C ₅ H ₁₁ ONa
		<i>n</i> -C ₇ H ₁₅ COCH ₃	<i>t</i> -C ₄ H ₉ OK
		<i>i</i> -C ₄ H ₉ COC ₄ H ₉ - <i>i</i>	NaOC ₂ H ₅
			<i>t</i> -C ₄ H ₉ OK
			

 α -HALONITRILE-STABILIZED CARBANIONS WITH ALDEHYDES AND KETONES (Continued)

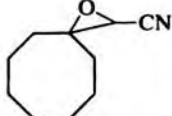
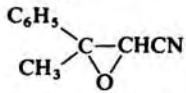
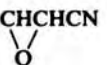
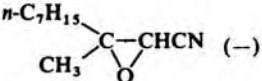
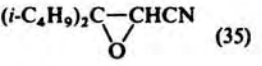
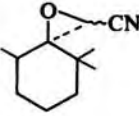
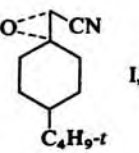
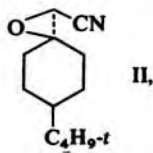
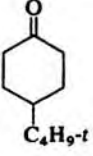
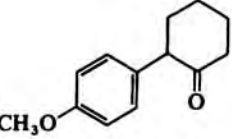
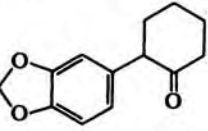
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
Et ₂ O, 0°	 (-)	520
HMPA —	 (E:Z = 45:55) (-)	503 528
—	" (80)	526
—	" (78)	530
Et ₂ O Et ₂ O, -10° <i>t</i> -C ₄ H ₉ OH <i>t</i> -C ₄ H ₉ OH C ₆ H ₆	" (-) " (80) E:Z = 64:36 (50) E:Z = 63:37 (60) E:Z = 68:32 (5)	509,510 513,927 503 503 503
Xylene, -10°	3,4-(CH ₃ O) ₂ C ₆ H ₃ CHCHCN  (-)	522,523
Et ₂ O, 0°	<i>n</i> -C ₇ H ₁₅  (-)	520
Et ₂ O, -10°	(<i>i</i> -C ₄ H ₉) ₂ C-CHCN  (35)	514
<i>t</i> -C ₄ H ₉ OH		518
	 I,  II	

TABLE XXXII. DARZENS GLYCIDONITRILE SYNTHESIS: REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile	Base
C ₂ (Contd.)	ClCH ₂ CN		Base ^a Base ^a Base ^a RZnBr ^a RZnBr ^a RLi ^a RLi ^a <i>t</i> -C ₄ H ₉ OK
		α -Tetralone	"
		"	<i>t</i> -C ₅ H ₁₁ ONa
		<i>n</i> -C ₉ H ₁₉ COCH ₃	<i>t</i> -C ₄ H ₉ OK
		FcCHO	NaOC ₂ H ₅
		Cyclododecanone	<i>t</i> -C ₄ H ₉ OK
		4- <i>i</i> -C ₄ H ₉ C ₆ H ₄ COCH ₃	<i>i</i> -C ₃ H ₇ ONa
		"	NaOH
			NaH
			50% aq NaOH, 18-crown-6
C ₆ H ₅ COC ₆ H ₅	50% aq NaOH, [C ₆ H ₅ CH ₂ N(C ₂ H ₅) ₃]Cl		

 α -HALONITRILE-STABILIZED CARBANIONS WITH ALDEHYDES AND KETONES (Continued)

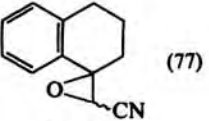
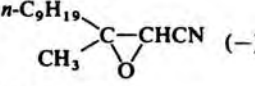
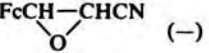
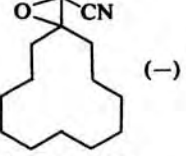
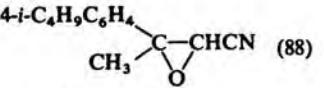
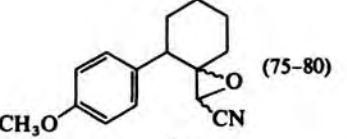
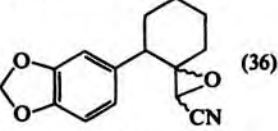
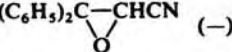
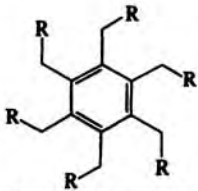
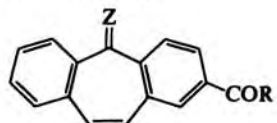
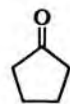
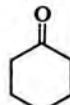
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
HMPA	I:II = 60:40 (-)	840
THF	I:II = 50:50 (-)	840
Et ₂ O	I:II = 50:50 (-)	840
THF	I:II = 33:67 (73)	841
THF, HMPT	I:II = 28:72 (52)	841
Pentane, Et ₂ O	I:II = 35:65 (67)	841
C ₆ H ₆ , HMPT	I:II = 35:65 (53)	841
Et ₂ O, 0°	I:II (-)	520
<i>t</i> -C ₄ H ₉ OH	 (77)	518
—	" (>95)	521
Et ₂ O, 0°	 (-)	520
Et ₂ O, -60°	 (-)	517
Et ₂ O, 0°	 (-)	520
Xylene, -10°	 (88)	521-524
Toluene and DMF or DMSO or CH ₃ C(O)N(CH ₃) ₂ or HMPA	" (88)	508
DME	 (75-80)	506
C ₆ H ₆	 (36)	531
—	 (-)	526

TABLE XXXII. DARZENS GLYCIDONITRILE SYNTHESIS: REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile	Base
C ₂ (Contd.)	ClCH ₂ CN	C ₆ H ₅ COC ₆ H ₅	50% aq NaOH, 
		"	R = S(CH ₂) ₂ O(CH ₂) ₂ O(CH ₂) ₂ OCH ₃ NaOC ₂ H ₅
		3,4-F(C ₆ H ₅)C ₆ H ₃ COCH ₃	<i>t</i> -C ₅ H ₁₁ ONa
		C ₆ H ₅ CH ₂ COCH ₂ C ₆ H ₅	NaOC ₂ H ₅
		(4-CH ₃ C ₆ H ₄) ₂ CO	"
			NaOCH ₃
		Estrone 3-methyl ether	<i>t</i> -C ₄ H ₉ OM or MNH ₂ where M = K, Na, etc.
C ₃	CH ₂ =C(Cl)CN	<i>n</i> -C ₃ H ₇ CHO	KOCH ₂ CH=CH ₂
	CH ₃ CH(Cl)CN	<i>i</i> -C ₃ H ₇ COCH ₃	<i>t</i> -C ₄ H ₉ OK
	CH ₂ =C(Cl)CN		NaOCH ₃
	CH ₃ CH(Cl)CN		<i>t</i> -C ₄ H ₉ OK

 α -HALONITRILE-STABILIZED CARBANIONS WITH ALDEHYDES AND KETONES (Continued)

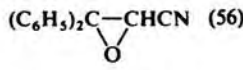
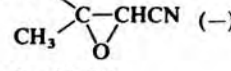
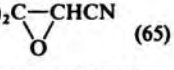

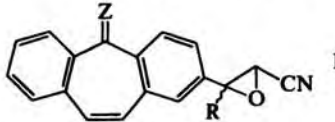
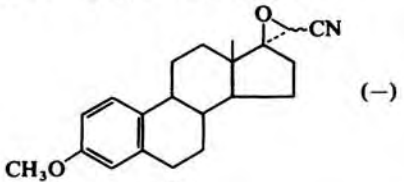
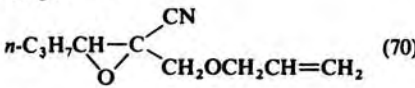
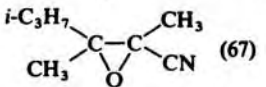
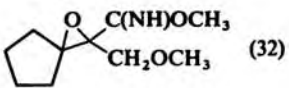
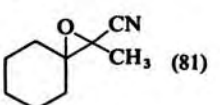
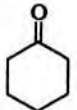
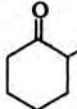
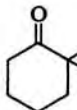
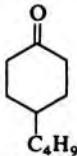
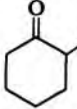
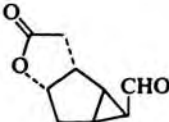
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
—	 (56)	530
Et ₂ O, 0°	" (84)	512,514
Xylene, -10°	3,4-F(C ₆ H ₅)C ₆ H ₃  (—)	523
Et ₂ O, -10°	(C ₆ H ₅ CH ₂) ₂ C-CHCN  (65)	514
"	(4-CH ₃ C ₆ H ₄) ₂ C-CHCN  (80)	514
THF	 I I R = CH ₃ , Z = O (39) I R = H, Z = O (—) I R = CH ₃ , Z = O(CH ₂)O (—)	511
—	 (—)	519
—	<i>n</i> -C ₃ H ₇ CH-  (70)	123
<i>t</i> -C ₄ H ₉ OH	<i>i</i> -C ₃ H ₇ -  (67)	518
CH ₃ OH	 (32)	123
<i>t</i> -C ₄ H ₉ OH	 (81)	518

TABLE XXXII. DARZENS GLYCIDONITRILE SYNTHESIS: REACTIONS OF

No. of C Atoms	Nucleophile	Electrophile	Base
C ₃ (Contd.)	CH ₂ =C(Cl)CN		NaOCH ₃
	CH ₃ CH(Cl)CN		<i>t</i> -C ₄ H ₉ OK
	CH ₂ =C(Cl)CN	C ₆ H ₅ CHO	NaOCH ₃
	CH ₃ CH(Cl)CN		<i>t</i> -C ₄ H ₉ OK
			Base ^a
			NaH
	CH ₂ =C(Cl)CN	C ₆ H ₅ COC ₆ H ₅	NaOCH ₃
C ₇	<i>n</i> -C ₅ H ₁₁ CBBr ₂ CN		P[N(CH ₃) ₂] ₃
C ₈	C ₆ H ₅ CHClCN	C ₆ H ₅ CHO	NaOH, [(<i>n</i> -C ₄ H ₉) ₄ N]Br <i>t</i> -C ₄ H ₉ ONa <i>t</i> -C ₄ H ₉ ONa LiN[Si(CH ₃) ₃] ₂ <i>t</i> -C ₄ H ₉ OK <i>t</i> -C ₄ H ₉ ONa LiN[Si(CH ₃) ₃] ₂ NaH <i>t</i> -C ₄ H ₉ ONa

^a The base was not specified. α -HALONITRILE-STABILIZED CARBANIONS WITH ALDEHYDES AND KETONES (Continued)

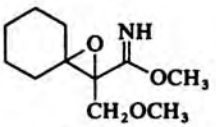
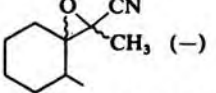
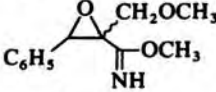
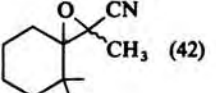
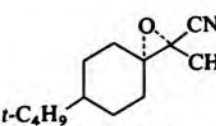
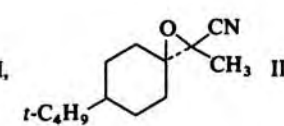
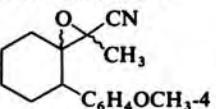
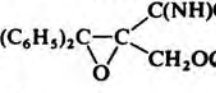
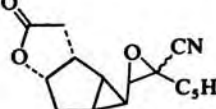
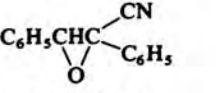
Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
CH ₃ OH	 (85)	123
<i>t</i> -C ₄ H ₉ OH	 (-)	518
CH ₃ OH	 (80)	123
<i>t</i> -C ₄ H ₉ OH	 (42)	518
HMPA	 I,  II I:II = 20:80 (-)	840
DME	 (75)	506
CH ₃ OH	 (7)	123
THF, -15°	 (97)	121
—		
HMPA	Z:E = 98:2 (95)	529
C ₆ H ₆	Z:E = 98:2 (95)	529,533
"	Z:E = 25:75 (70)	529,533
"	Z:E = 98:2 (35)	529,533
THF	Z:E = 80:20 (70)	529,533
THF	Z:E = 70:30 (70)	529,533
THF	Z:E = 98:2 (95)	529,533
HMPA	Z:E = 98:2 (-)	529
THF	Z:E = 80:20 (-)	529

TABLE XXXIII. TANDEM CONJUGATE ADDITION-ALKYLATION OF α -HALOACRYLONITRILES

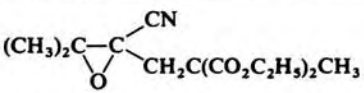
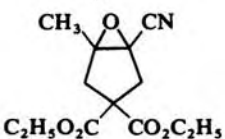
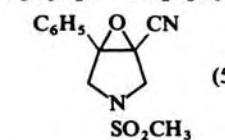
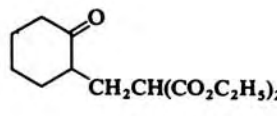
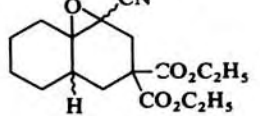
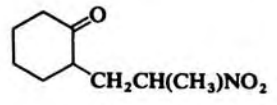
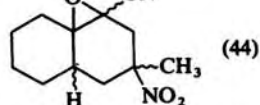
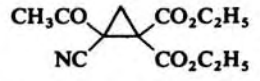
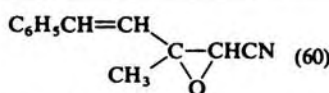
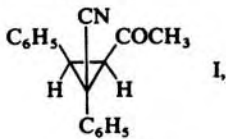
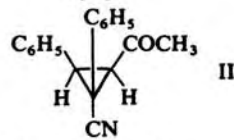
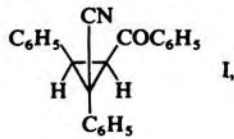
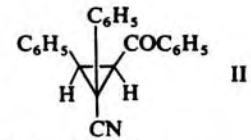
No. of C Atoms	Acceptor	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃	CH ₂ =C(Cl)CN	CH ₃ CH(CO ₂ C ₂ H ₅) ₂	CH ₃ COCH ₃	<i>t</i> -C ₄ H ₉ OK	C ₆ H ₆	 (57)	125
"	"	CH ₃ COCH ₂ CH(CO ₂ C ₂ H ₅) ₂	—	"	"	 (61)	125
"	"	C ₆ H ₅ COCH ₂ NHSO ₂ CH ₃	—	"	"	 (50)	125
"	"		—	"	"	 (54)	125
"	"		—	"	"	 (44)	125
"	"	CH ₃ COCH(CO ₂ C ₂ H ₅) ₂	—	"	"	 (71)	125

TABLE XXXIV. INTRAMOLECULAR REACTIONS OF α -HALONITRILE-STABILIZED ANIONS

No. of C Atoms	Nucleophile	Electrophile	Base	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂	ClCH ₂ CN	C ₆ H ₅ CH=CHCOCH ₃	NaH	HMPA	 C ₆ H ₅ CH=CH-C(CH ₃)(O)-CHCN (60)	507
		"	<i>t</i> -C ₄ H ₉ OK NaN[Si(CH ₃) ₃] ₂	HMPA or Et ₂ O THF	" (60) " (60-70)	507 507
C ₈	C ₆ H ₅ CHClCN	C ₆ H ₅ CH=CHCOCH ₃	<i>t</i> -C ₄ H ₉ OK or LiN[Si(CH ₃) ₃] ₂	—	 I,	507
		C ₆ H ₅ CH=CHCOCH ₃	"	—	 II,	
		C ₆ H ₅ CH=CHCOC ₆ H ₅	"	—	I:II = 50:50 (—)	
		C ₆ H ₅ CH=CHCOC ₆ H ₅	"	—	 I,	507
		C ₆ H ₅ CH=CHCOC ₆ H ₅	"	—	 II,	
		C ₆ H ₅ CH=CHCOC ₆ H ₅	"	—	I:II = 50:50 (—)	

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