ences of chemical shifts of methoxy methyl protons and methyl protons on silicon were utilized in the determination, and amounts of each isomers were calculated from the peak area of protons.

2. **Benzene–Hexadeuteriobenzene.** A mixture of carefully weighed benzene and hexadeuteriobenzene was made and an aliquot was saved. The remainder was added to the hydrosilane, followed by introduction of DTBP. In this manner, each of five solutions was prepared for pentamethyldisilane and *n*-propyldimethylsilane of varying concentration. Each mixture was allowed to react in the same way described above. From the reaction mixtures, phenylsilanes were separated by glc.

Mass spectra of phenylsilanes were obtained with a Hitachi RMU-6D mass spectrometer, the ionizing energy being maintained at 70 eV. The analyses of phenylpentamethyldisilane–pentadeuteriophenylpentamethyldisilane mixtures were carried out by comparing the relative intensity of the molecular ions, $(C_6H_5Si_2Me_5)^+$ at *m/e* 208 and $(C_6D_5Si_2Me_5)^+$ at *m/e* 213. The fragment ions at *m/e* 193 and 135 were also compared to the corresponding ions at *m/e* 198 and 140. The results were in good agreement and were averaged. The molar ratio of reactants had little effect on the k_H/k_D values.

By comparing the relative intensity of ions at *m/e* 178, 163, 135, and 121 from *n*-propyldimethylsilane with the corresponding ions at *m/e* 183, 168, 140, and 126 from the deuterated compound, the k_H/k_D was calculated.

The same approach was used to determine the k_H/k_D of cyclohexylation by comparing the relative intensity of ions at *m/e* 160, 117, and 91 with the corresponding peaks at *m/e* 165, 122, and 96.

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Polylithium Compounds. IV. Polylithiation of Nitriles and the Preparations of Trisilyl Ynamines[1,2]

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Abstract: Acetonitrile reacts with excess *tert*-butyllithium in ether at −78° to form Li_2C_2HN and 2 equiv of isobutane. With aldehydes and ketones, Li_2C_2HN gives diadducts, $(LiOCR_2)_2CHCN$, in high yields. These adducts are converted to the corresponding trimethylsilyl derivatives with trimethylchlorosilane. Li_2C_2HN, in the presence of excess base, and trimethylchlorosilane in tetrahydrofuran give a mixture of tris(trimethylsilyl)ethynylamine (**9**) and tris(trimethylsilyl)ketenimine (**1**). Li_2C_2HN also reacts with *tert*-butyldimethylchlorosilane and dimethylchlorosilane to give the corresponding trisilyl ynamines and ketenimines. Trisilyl ynamines undergo a quantitative thermal rearrangement to trisilyl ketenimines. Trimethylsilylacetonitrile and bis(trimethylsilyl)acetonitrile react with *n*-butyllithium forming a dilithium derivative, $Li_2(Me_3Si)C_2N$, and a monolithium derivative, $Li(Me_3Si)_2C_2N$, respectively. The structures of the metalated nitriles were investigated by infrared spectroscopy.

An isoelectronic series of linear species containing 16 valence electrons (the carbon dioxide structure) is known in inorganic chemistry (Table I).[3] It has been shown that propyne reacts with excess *n*-butyllithium to form the perlithio compound C_3Li_4.[2,4] This compound can be regarded formally as a derivative of the linear trianion C_3^{4-}, isoelectronic with carbon dioxide. If this formalism is used, Table I shows that there is a gap at −3 charge. The trilithium derivatives of acetonitrile or methylisocyanide[5] could be considered members of this series and would serve to fill in the gap at −3 charge.

Table I. Isoelectronic Species with 16 Valence Electrons

Charge	Species
+1	NO_2^+
0	CO_2, N_2O, CS_2, FCN
−1	NCO^-, NCS^-, N_3^-, CNO^-
−2	NCN^{2-}
−3	
−4	(CCC^{4-})

Metalation of Acetonitrile. Acetonitrile readily reacts with 1 equiv of *N*-sodiohexamethyldisilazane[6] or 1 equiv of *n*-butyllithium in tetrahydrofuran (THF)[7,8] to give monometalated derivatives. The possible formation of trimetalated derivatives from the reaction of acetonitrile with 3 equiv of these bases has been reported also.[7,9] The existence of trimetalated acetonitriles was based solely on the isolation of trialkyl and trisilyl derivatives of acetonitrile from reactions of the metalated nitriles with alkyl halides and trimethylchlorosilane.

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[1] This work was supported in part by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, USAF, Grant No. AF-AFOSR-69-1772. Grateful acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support.

[2] Previous paper in this series: R. West and P. C. Jones, *J. Amer. Chem. Soc.*, **91**, 6156 (1969).

[3] H. A. Bent, *J. Chem. Educ.*, **43**, 170 (1966).

[4] R. West, P. A. Carney, and I. C. Mineo, *J. Amer. Chem. Soc.*, **87**, 3788 (1965).

[5] R. West and G. A. Gornowicz, submitted for publication.

[6] C. Kruger, *J. Organometal. Chem.*, **9**, 125 (1967).

[7] E. M. Kaiser and C. R. Hauser, *J. Org. Chem.*, **33**, 3402 (1968).

[8] D. N. Crouse and D. Seebach, *Chem. Ber.*, **101**, 3113 (1968).

[9] C. Kruger and E. G. Rochow, *Angew. Chem.*, **75**, 793 (1963); *Angew. Chem., Int. Ed. Engl.*, **2**, 617 (1963).

$$\mathrm{CH_3CN + 3NaN(SiMe_3)_2 \xrightarrow{Et_2O} \underset{solid}{\text{“}Na_3CCN\text{”}}} \qquad (1)$$

$$\mathrm{\underset{solid}{\text{“}Na_3CCN\text{”}} + Me_3SiCl \longrightarrow \underset{\textbf{1},\ quant}{(Me_3Si)_2C{=}C{=}NSiMe_3}}$$

$$\mathrm{\underset{solid}{\text{“}Na_3CCN\text{”}} + MeI \longrightarrow Me_3CCN}$$

$$\mathrm{CH_3CN + 3\mathit{n}\text{-}BuLi \xrightarrow{THF} \text{“}Li_3CCN\text{”} \xrightarrow{PhCH_2Cl} (PhCH_2)_3CCN} \qquad (2)$$

However, these reactions do not give trimetalated derivatives of acetonitrile but only monometalated derivatives. As reported[9] the reaction of acetonitrile with 3 equiv of *N*-sodiohexamethyldisilazane gives a white, ether-insoluble solid. When this solid is filtered from any unreacted base and then derivatized with trimethylchlorosilane, tris(trimethylsilyl)ketenimine (**1**) is formed in low yield only. Bis(trimethylsilyl)acetonitrile (**2**) and trimethylsilylacetonitrile (**3**) are isolated also.[10] Compounds **1**, **2**, and **3** are obtained also from the reaction of monolithioacetonitrile with trimethylchlorosilane. Treating the filtrate with trimethylchlorosilane gives 1.5 equiv of tris(trimethylsilyl)amine (**4**) and 1 equiv of hexamethyldisilazane (**5**). These products can only be formed by the reactions written in eq 3 and 4. The white solid, $\mathrm{NaCH_2CN}$, reacts with benzophenone to give, after aqueous workup, 3,3-diphenyl-3-hydroxypropanenitrile in high yield, further substantiating that the solid is only a monosodium and not a trisodium derivative of acetonitrile.

$$\mathrm{CH_3CN + 3NaN(SiMe_3)_2 \xrightarrow{Et_2O} \underset{solid}{NaCH_2CN} + \underset{\textbf{5}}{HN(SiMe_3)_2} + 2NaN(SiMe_3)_2} \qquad (3)$$

$$\mathrm{NaCH_2CN + Me_3SiCl \longrightarrow \underset{\textbf{1}}{(Me_3Si)_2C{=}C{=}NSiMe_3} + \underset{\textbf{2}}{(Me_3Si)_2CHCN} + \underset{\textbf{3}}{Me_3SiCH_2CN}} \qquad (4)$$

$$\mathrm{NaN(SiMe_3)_2 + Me_3SiCl \longrightarrow \underset{\textbf{4}}{(Me_3Si)_3N}}$$

$$\mathrm{NaCH_2CN + Ph_2C{=}O \longrightarrow \xrightarrow{H^+\text{-}H_2O} Ph_2(HO)CCH_2CN}$$

Acetonitrile and 3 equiv of *n*-butyllithium in THF at −78° give, after quenching with benzyl chloride, tribenzylacetonitrile in low yield.[7] Only 1 equiv of *n*-butane is formed prior to derivatization. Tribenzylacetonitrile must be formed by sequential metalation and benzylation, *vide infra.*

Acetonitrile and 3 equiv of *tert*-butyllithium in ether at −78° give a pale yellow solution from which a white solid slowly precipitates. After 16 hr, 1.8 equiv of isobutane is obtained (no isobutane is formed from *tert*-butyllithium and ether under these conditions).

$$\mathrm{CH_3CN + 3\mathit{tert}\text{-}BuLi \longrightarrow Li_2C_2HN + 2isobutane}$$

Increasing the reaction time or amount of *tert*-butyllithium does not increase the amount of isobutane formed. With 6 or more equiv of *tert*-butyllithium the lithiated acetonitrile remains in solution indefinitely (the metalated nitrile probably forms a soluble complex with excess *tert*-butyllithium). Therefore metalation is not stopped because the partially metalated nitrile is insoluble. With 2 equiv of *tert*-butyllithium a white solid forms immediately and only about 1.4 equiv of isobutane is liberated.

The isolation of 2 equiv of isobutane from the reaction of acetonitrile with excess *tert*-butyllithium strongly implies that the solid is a dilithium derivative of acetonitrile, $\mathrm{Li_2C_2HN}$. This implication is verified by the reactions of the solid with aldehydes and ketones to give diadducts, $\mathrm{(LiOCR_2)_2CHCN}$, in high yield. Acetaldehyde and the solid give a mixture of $\mathrm{LiOCHMeCH_2CN}$, $\mathrm{(LiOCHMe)_2CHCN}$, and $\mathrm{(LiOCHMe)_3CCN}$. These adducts were isolated after conversion to the corresponding trimethylsilyl derivatives with trimethylchlorosilane. In a similar manner acetone and the solid, followed by quenching with trimethylchlorosilane, give 2,4-dimethyl-2,4-bis(trimethylsiloxy)-3-cyanopentane.

$$\mathrm{CH_3CN + 3\mathit{tert}\text{-}BuLi \xrightarrow{Et_2O} \xrightarrow{CH_3C(O)H} \begin{array}{l} LiOCHMeCH_2CN \\ (LiOCHMe)_2CHCN \\ (LiOCHMe)_3CCN \end{array}}$$

$$\Big\downarrow \mathrm{Me_3SiCl}$$

$$\mathrm{\underset{\textbf{6},\ 10\%}{Me_3SiOCHMeCH_2CN} + \underset{\textbf{7},\ 70\%}{(Me_3SiOCHMe)_2CHCN} + \underset{\textbf{8},\ 5\%}{(Me_3SiOCHMe)_3CCN}}$$

Formation of **8** in the above reaction is not evidence for the existence of a trilithio derivative of acetonitrile. **8** is most likely formed by metalation of either $\mathrm{(LiOCHMe)LiC_2HN}$ or $\mathrm{(LiOCHMe)_2CHCN}$ by excess *tert*-butyllithium during the derivatization. If the organolithium solution is warmed to room temperature prior to the addition of acetaldehyde, in order to destroy the excess *tert*-butyllithium by metalation of ether solvent, *only* **7** *is obtained.* With 6 equiv of *tert*-butyllithium compounds, **7** and **8** are obtained in equal amounts but only 2 equiv of isobutane is obtained prior to derivatization with acetaldehyde.

Trisilyl Ynamines. $\mathrm{Li_2C_2HN}$, in the presence of excess base, and trimethylchlorosilane in THF give not only the known ketenimine **1** but also the new tris(trimethylsilyl)ethynylamine (**9**). Ynamine **9** is a colorless liquid, showing a strong C≡C stretching absorption at 2140 cm^{-1} in the ir spectrum and two trimethylsilyl singlets in the nmr spectrum, ratio 2:1. The total yield of **9** and **1** is usually *ca.* 85%, but the ratio of **9** to **1** is dependent on the conditions of derivatization. If no THF is present only a trace of **9** is formed. In a mixture of equal amounts of THF and ether the yield of **9** is increased to 20%, and if all the ether is replaced by THF the yield of **9** is increased to 50%.

$$\mathrm{CH_3CN + 3\mathit{tert}\text{-}BuLi \xrightarrow[-78^\circ]{Et_2O} \xrightarrow[THF]{Me_3SiCl} \underset{\textbf{9},\ 20\%}{Me_3SiC{\equiv}CN(SiMe_3)_2} + \underset{\textbf{1},\ 80\%}{(Me_3Si)_2C{=}C{=}NSiMe_3}}$$

tert-Butyldimethylchlorosilane and $\mathrm{Li_2C_2HN}$ in THF–ether solvent at −78° give tris(*tert*-butyldimethylsilyl)ethynylamine (**10**), $\mathrm{\mathit{tert}\text{-}BuMe_2SiC{\equiv}CN(SiMe_2\text{-}\mathit{tert}\text{-}Bu)_2}$, and tris(*tert*-butyldimethylsilyl)ketenimine (**11**), $\mathrm{(\mathit{tert}\text{-}BuMe_2Si)_2C{=}C{=}NSiMe_2\text{-}\mathit{tert}\text{-}Bu}$, in 83%

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[10] Infrared analysis shows that acetonitrile and an unidentified nitrile are also present in the crude product.

total yield, the ratio of **10** to **11** being *ca.* 2:1. Dimethylchlorosilane and Li_2C_2HN give tris(dimethylsilyl)ethynylamine (**12**), and tris(dimethylsilyl)ketenimine (**13**), in 80% total yield. The ratio of **12** to **13** was *ca.* 1:2. In the latter reaction Li_2C_2HN was added to excess dimethylchlorosilane in THF at −78° to minimize attack at the silicon–hydrogen bond.

Unlike organic ynamines,[11] trisilyl ynamines are thermally unstable. Ynamines **9** and **12** rearrange quantitatively to the corresponding ketenimines **1** and **13** within 24 hr at 160°. Ynamine **10** is unchanged

$$R_3SiC{\equiv}CN(SiR_3)_2 \xrightarrow[160^\circ]{\circ} (R_3Si)_2C{=}C{=}NSiR_3$$

$$\mathbf{9},\ R_3Si = Me_3Si \qquad \mathbf{1},\ R_3Si = Me_3Si$$

$$\mathbf{12},\ R_3Si = HMe_2Si \qquad \mathbf{13},\ R_3Si = HMe_2Si$$

under these conditions but is converted quantitatively to ketenimine **11** when heated at 250° for 7 days in a sealed tube. Ynamine **9** even rearranges slowly to ketenimine **1** at room temperature.

In order to study the chemistry of these new silyl ynamines, better methods of preparation are needed, preferably ones which give no ketenimine isomers. So far we have been unable to prepare silyl ynamines by conventional routes[11] used to prepare organic ynamines. Chloroethynyltrimethylsilane and *N*-sodiohexamethyldisilazane give only tris(trimethylsilyl)amine (**4**) and black tar. Compound **4** may be formed by

$$ClC{\equiv}CSiMe_3 + NaN(SiMe_3)_2 \longrightarrow \underset{\mathbf{4},\ 65\%}{(Me_3Si)_3N}$$

nucleophilic attack of nitrogen on silicon in chloroethynyltrimethylsilane.[12] However, the same product

$$(Me_3Si)_2N^- + Me_3SiC{\equiv}CCl \longrightarrow \underset{\mathbf{4}}{(Me_3Si)_3N} + (ClC{\equiv}C^-)$$

is obtained from chloroethynylbenzene and *N*-sodiohexamethyldisilazane. Obviously, the above mech-

$$PhC{\equiv}CCl + NaN(SiMe_3)_2 \longrightarrow \underset{\mathbf{4},\ 55\%}{(Me_3Si)_3N}$$

anism cannot be operative in this reaction, but a plausible pathway for the formation of **4** from these reagents cannot be suggested presently.

Metalation of Other Nitriles. *n*-Alkyllithiums and alkylacetonitriles give addition products in high yields.[13] *N*-Sodiohexamethyldisilazane and propanenitrile give $MeCH_2C({=}NNa)CHMeCN$,[6] metalation of propanenitrile being slow compared to the dimerization reaction. *tert*-Butyllithium and propanenitrile in pentane at −78° give mainly the addition product LiN=C(Et)-*tert*-Bu. Only 0.2 equiv of isobutane was evolved. After quenching the reaction with trimethylchlorosilane 2,2-dimethyl-3-trimethylsilyliminopentane[14] (**14**) and methyltrimethylsilyl-*N*-trimethylsilylketenimine (**15**) are obtained in the ratio 9:1. The ratio **15**:**14** was increased to *ca.* 1:2 by complexing the *tert*-butyllithium with *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) before addition of propanenitrile.

$$MeCH_2CN + 2\textit{tert}\text{-}BuLi \longrightarrow \xrightarrow{Me_3SiCl}$$

$$\underset{\mathbf{14}}{Me_3SiN{=}C(Et)\text{-}\textit{tert}\text{-}Bu} + \underset{\mathbf{15}}{Me_3Si(Me)C{=}C{=}NSiMe_3}$$

Isobutanenitrile and *tert*-butyllithium also give an addition product, $LiN{=}C(CHMe_2)CMe_3$. Derivatization with trimethylchlorosilane gives 2,2,4-trimethyl-3-trimethylsilyliminopentane in 82% yield.

For metalation to compete favorably with addition in reactions of substituted acetonitriles with organolithium compounds, the substituents must be more electron withdrawing than alkyl groups are. Phenylacetonitrile is metalated readily with *n*-butyllithium to give a dilithium derivative.[15] Trimethylsilylacetonitrile and *n*-butyllithium also yield a dilithium derivative, $Me_3SiC_2Li_2N$, and 2 equiv of *n*-butane; quenching with trimethylchlorosilane in THF gives a 4:1 mixture of ketenimine **1** and ynamine **9**. Bis(trimethylsilyl)acetonitrile and *n*-butyllithium give a monolithium derivative, $Li(Me_3Si)_2C_2N$, derivatization with trimethylchlorosilane giving only **1**.

Infrared Spectra and Structures of Metalated Nitriles. Infrared spectroscopy provides important information concerning the structures of metalated nitriles. Table II shows that the monolithium and monosodium derivatives of acetonitrile have more than one absorption in the region 2400–1600 cm^{-1}. These derivatives must exist in more than one tautomeric structure. The

Table II. Absorption Bands in the 1600–2400-cm^{-1} Region for Metalated Nitriles

Compd	Frequency, cm^{-1}
$NaC_2H_2N^a$	2240, 2160, 2050
NaC_2HPhN^a	2080
$LiC_2H_2N^b$	2130, 2040
$LiC_2Me_2N^c$	2000
$LiC_2(Me_3Si)_2N^d$	2000
$Li_2C_2HN^e$	1820
$Li_2C_2MeN^d$	1880
$Li_2C_2PhN^c$	1900
$Li_2C_2(Me_3Si)N^d$	1900

[a] Reference 6; in KBr pellet, pyridine, or benzene solution. [b] Suspension in THF–hexane. [c] Solution in hexane. [d] Suspension in pentane or hexane. [e] Suspension in ether.

$$MCH_2CN \rightleftharpoons MCH{=}C{=}NH \rightleftharpoons MC{\equiv}CNH_2 \rightleftharpoons HC{\equiv}CNMH \rightleftharpoons H_2C{=}C{=}NM$$

monolithium species, $Li(Me_3Si)_2C_2N$ and $LiMe_2C_2N$, show only one absorption at 2000 cm^{-1}. This absorption is probably too high to be a lithiated ketenimine, $R_2C{=}C{=}NLi$, and these species probably exist in the form R_2LiCCN. Kruger[6] reported that the monosodium derivative of phenylacetonitrile exists only in the form PhCHNaCN.

All the dilithiated nitriles show one absorption between 1900 and 1800 cm^{-1}. These compounds also could occur in several tautomeric forms. When R is

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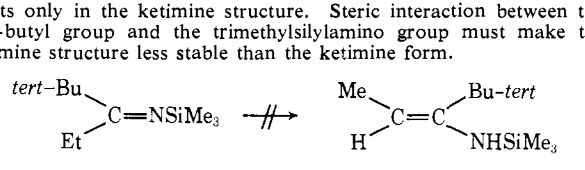
(11) H. G. Viehe *Angew. Chem.*, **79**, 744 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 767 (1967).

(12) This is a typical reaction of ethynylsilanes with nucleophilic reagents; see C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p 143.

(13) G. Sumrell, *J. Org. Chem.*, **19**, 817 (1954).

(14) L. H. Chan and E. G. Rochow (*J. Organometal. Chem.*, **9**, 231 (1967)) found that *N*-silylketimines with a hydrogen in the α position readily tautomerize to enamines. Nmr and ir spectra show that **14** exists only in the ketimine structure. Steric interaction between the *tert*-butyl group and the trimethylsilylamino group must make the enamine structure less stable than the ketimine form.



(15) E. M. Kaiser and C. R. Hauser, *J. Amer. Chem. Soc.*, **88**, 2348 (1966).

$$RCLi_2CN \rightleftharpoons RLiC{=}C{=}NLi \rightleftharpoons RC{\equiv}CNLi_2$$

hydrogen, more tautomeric forms similar to those of monometalated acetonitriles can be written. These frequencies are too low to be acetylenic or nitrile absorptions and indicate that the dilithium species are ketenimine derivatives, $R(Li)C{=}C{=}NLi$. If the dilithiated nitriles are considered to be ionic species it is possible to write a delocalized structure $(RC\overset{\cdot\cdot}{=}C\overset{\cdot\cdot}{=}N)^{2-}$. Klein and Brenner have called this structure a sesquiazacetylene.[16]

"Trilithium" Derivatives of Acetonitrile. Attempts to prepare a trilithium derivative of acetonitrile have been unsuccessful so far. Potentiating agents such as TMEDA or THF in ether at −78° give only 2 equiv of isobutane and Li_2C_2HN. Potassium *tert*-butoxide causes the *tert*-butyllithium to metalate the ether solvent at −78° before the last proton is removed from Li_2C_2HN.[17] Solvent is also metalated when the reaction is warmed above −20°. Tertiary amines are more difficult to metalate than ethers are, but triethylamine, used as solvent, is metalated before the final proton is removed from Li_2C_2HN. Hydrocarbon solvents such as pentane and benzene give complex mixtures of products.

It is of interest to compare lithiation of acetonitrile with that of propyne. When propyne is treated with 2 or 3 equiv of *n*-butyllithium, a mixture of LiC_3H_3, $Li_2C_3H_2$, Li_3C_3H, and Li_4C_3 is obtained.[2] There appears to be little build up of charge on the C_3 moiety by the introduction of more lithium atoms. Therefore, replacement of hydrogen by lithium is about as facile for the fourth proton as it is for the second. With acetonitrile, the first proton is removed more easily than the second which in turn is removed more easily than the third. The increased difficulty in replacing the protons of acetonitrile with lithium atoms is probably caused by the formation of a lithium–nitrogen bond. The lithium–nitrogen bond is more ionic than the lithium–carbon bond and the increased charge on the C_2N moiety decreases the acidity of the last proton.

The trisilyl ketenimines must be formed by a process of metalation during the derivatization and not from trimetalated derivatives of acetonitrile. This process is

$$MCH_2CN + Me_3SiCl \longrightarrow Me_3SiCH_2CN \xrightarrow{\text{base}}$$

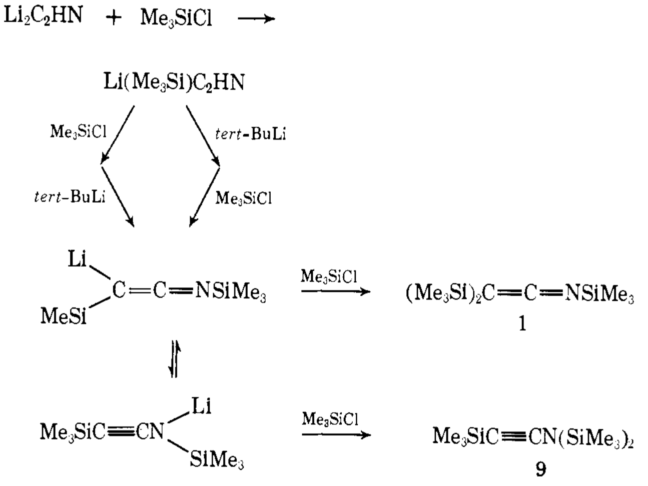
$$Me_3SiCH(M)CN \xrightarrow{Me_3SiCl} (Me_2Si)_2CHCN \xrightarrow{\text{base}}$$

$$(Me_3Si)_2C(M)CN \xrightarrow{Me_3SiCl} \underset{\mathbf{1}}{(Me_3Si)_2C{=}C{=}NSiMe_3}$$

$$M = Na \text{ or } Li$$

greatly enhanced by the strong acidifying effect of silicon on α protons.[18] In the above reactions the base may be excess metalating agent, for example, *N*-sodiohexamethyldisilazane, *n*- or *tert*-butyllithium, or a metalated acetonitrile derivative such as $NaCH_2CN$, $LiCH_2CN$, $Me_3SiCH(Li)CN$, or $Me_3SiCH(Na)CN$.

The formation of trisilyl ynamines from chlorosilanes and Li_2C_2HN must occur by a similar but more complex process.



The actual reaction is probably much more complicated than the above simplified scheme. Many of the intermediates are also capable of existing in tautomeric forms and the final products may depend on the stability and reactivity of these intermediates, and not just on the last two tautomeric structures written above.

Trialkylation of mono- and dimetalated acetonitriles most likely occurs by the same process. Alkyl groups do not increase the acidity of the α protons as silyl groups do, but the coupling reaction with alkyl halides is very slow enabling metalation to occur during derivatization. Consequently the yields of trialkylacetonitriles are quite low compared to the yields of trisilyl derivatives of acetonitrile.

Experimental Section

All reactions involving organolithium compounds were carried out in an atmosphere of dry nitrogen. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nmr spectra were recorded on a Varian A-60 spectrometer. Gas chromatographic (gc) separations were made on a Varian Aerograph A-700 chromatograph using columns packed with either SE-30 or QF-1 silicone on Chromosorb W. Mass spectral molecular weights were obtained using an AEI Model MS-9 spectrometer. All boiling points and melting points are uncorrected. Infrared spectra were recorded on Perkin-Elmer Model 237 and Model 457 spectrometers. All liquid products were characterized after purification by preparative gc.

Trimethylsilylacetonitrile (**3**) was prepared by slowly adding 100 ml of 1.2 *M* *tert*-butyllithium in pentane to a solution of 38 ml (0.3 mol) of trimethylchlorosilane in 52 ml (1.0 mol) of acetonitrile at 0–10°. After filtering the inorganic salts, the filtrate was distilled (anhydrous work-up) to give 8 g of clear liquid, bp 80–130° at 50 Torr. Gc analysis showed this liquid to be a mixture of trimethylsilylacetonitrile (**3**) and tris(trimethylsilyl)ketenimine (**1**), ratio *ca.* 2:1. Purification by preparative gc gave 3 g of **3**, $n^{24}\mathrm{D}$ 1.4212 (lit.[19] $n^{20}\mathrm{D}$ 1.4203).

Hydrolysis of tris(trimethylsilyl)ketenimine (**1**) with dilute hydrochloric acid gave bis(trimethylsilyl)acetonitrile (**2**), $n^{22}\mathrm{D}$ 1.4492 (lit.[19] $n^{20}\mathrm{D}$ 1.4497).

All other reagents were either prepared by published procedures or obtained from commercial sources and purified prior to use if necessary.

Lithiation of Nitriles. A. Acetonitrile. Pentane was distilled from 100 ml of 1.2 *M* *tert*-butyllithium solution keeping the pot temperature below 45°. After cooling the *tert*-butyllithium in a Dry Ice–acetone bath, 50 ml of ether was added slowly. Then a solution of 1.75 ml (0.033 mol) of acetonitrile in 50 ml of ether was added dropwise to give a pale yellow solution, from which a white solid slowly precipitated. After 16 hr at −78°, part of the solvent was removed at −40 to −50° at 0.3 Torr and collected in a trap immersed in liquid nitrogen. Distillation of this condensate gave 4.0

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[16] J. Klein and S. Brenner, *J. Amer. Chem. Soc.*, **91**, 3094 (1969).

[17] M. Schlosser, *J. Organometal. Chem.*, **8**, 9 (1967).

[18] (a) D. J. Peterson, *ibid.*, **9**, 373 (1967); (b) G. A. Gornowicz and R. West, *J. Amer. Chem. Soc.*, **90**, 4478 (1968); (c) A. E. Bey and D. R. Weyenberg, *J. Org. Chem.*, **31**, 2036 (1966); (d) G. LeGrow and A. Moore, submitted for publication; (e) F. Jaffe, *J. Organometal. Chem.*, **23**, 53 (1970).

[19] M. Prober, *J. Amer. Chem. Soc.*, **78**, 2274 (1956).

Table III. Characterization of New Compounds

No.	Compound	n^tD	Infrared (neat), cm^{-1}	Nmr τ, CCl$_4$, TMS	*Anal.* Calcd	*Anal.* Found
6	$Me_3SiOCHMeCH_2CN$		2260 (CN)	6.0 (c, 1, CH)	C, 53.4	53.1
			1250 (Me_3Si)	7.67 (d, 2, CH_2)	H, 9.6	9.9
				8.72 (d, 3, Me)	N, 8.9	8.7
				9.87 (s, 9, Me_3Si)	Si, 17.8	17.4
7	$(Me_3SiOCHMe)_2CHCN$	n^{21} 1.4279	2250 (CN)	6.0 (c, 2, CH)	C, 52.9	53.2
			1250 (Me_3Si)	7.6 (c, 1, CHCN)	H, 9.9	10.2
				8.6 (c, 6, MeC)	N, 5.1	5.1
				9.88 (c, 18, Me_3Si)	Si, 20.5	20.0
8	$(Me_3SiOCHMe)_3CCN$		2240 (CN)	5.75 (c, 3, CH)	C, 52.4	52.6
			1250 (Me_3Si)	8.7 (c, 9, MeC)	H, 10.0	10.0
				9.87 (s, 27, Me_3Si)	N, 3.6	3.8
					Si, 21.6	21.9
9	$Me_3SiC{\equiv}CN(SiMe_3)_2$	n^{22} 1.4455	2140 ($C{\equiv}C$)	9.78 (s, 18, Me_3SiN)	C, 51.3	50.8
			1250 (Me_3Si)	9.93 (s, 9, Me_3SiC)	H, 10.6	10.3
					N, 5.4	5.6
					Si, 32.7	32.3
10	*tert*-$BuMe_2SiC{\equiv}CH(SiMe_2$-*tert*-$Bu)_2$		2140 ($C{\equiv}C$)	9.00 (s, 18, *tert*-BuSiN)	C, 62.7	62.5[a]
			1255 (Me_2Si)	9.10 (s, 9, *tert*-BuSiC)	H, 11.8	11.9
				9.77 (s, 12, Me_2SiN)	N, 3.7	3.5
				10.00 (s, 6, Me_2SiC)	Si, 22.0	22.0
11	(*tert*-$BuMe_2Si)_2C{=}C{=}NSiMe_2$-*tert*-Bu		2040 ($C{=}C{=}N$)	9.07 (s, 27, *tert*-BuSi)		
			1255 (Me_2Si)	9.83 (s, 6, Me_2SiN)		*a*
				9.92 (s, 12, Me_2SiC)		
13	$(HMe_2Si)_2C{=}C{=}NSiMe_2H$	n^{23} 1.4618	2140 (SiH)	5.42 (septet, 1, HSiH)	C, 44.6	44.8
			2020 ($C{=}C{=}N$)	5.83 (septet, 2, HSiC)	H, 9.8	9.7
			1260 ($SiMe_2$)	9.71 (d, 6, Me_2SiN)	N, 6.5	6.6
				9.84 (d, 12, Me_2SiC)	Si, 39.1	38.8
14	Et(*tert*-Bu)$C{=}NSiMe_3$	n^{20} 1.4296	1675 ($C{=}N$)	7.83 (q, 2, CH_2)	C, 64.8	64.5
			1250 (Me_3Si)	9.0 (t and s, 12, Me and CMe_3)	H, 12.5	12.3
				9.87 (s, 9, Me_3Si)	N, 7.5	7.4
					Si, 15.2	15.6
15	$Me(Me_3Si)C{=}C{=}NSiMe_3$		2000 ($C{=}C{=}N$)	8.54 (s, 3, CMe)	C, 54.2	54.0
			1250 (Me_3Si)	9.82 (s, 9, Me_3SiN)	H, 10.6	10.7
				9.95 (s, 9, Me_3SiC)	N, 7.0	6.9
					Si, 28.1	27.9
16	$Me_3SiOCHMeCMe_3$	n^{23} 1.4007	1250 (Me_3Si)	6.00 (q, 1, CH)	C, 62.0	61.8
				8.97 (d, 3, CMe)	H, 12.7	12.5
				9.17 (s, 9, CMe_3)	Si, 16.1	16.0
				9.93 (s, 9, Me_3Si)		
	$(Me_3SiOCMe_2)_2CHCN$	n^{23} 1.4374	2240 (CN)	7.46 (s, 1, CH)	C, 55.7	55.9
			1250 (Me_3Si)	8.50 (s, 12, Me_2C)	H, 10.3	10.3
				9.87 (s, 18, Me_3Si)	N, 4.6	4.4
					Si, 18.6	18.3

[a] Due to the difficulty of separating the ynamine from the ketenimine, chemical analyses were obtained from a mixture of the two isomers.

g of isobutane, 85% pure by gc (0.059 mol). THF (100 ml) and 20 ml (0.16 mol) of trimethylchlorosilane were added to the organolithium slurry. The mixture was warmed slowly to room temperature and filtered. Distillation of the filtrate gave 7.2 g (85%) of liquid, bp 65–70° at 1 Torr. Gc and nmr analyses showed this liquid to be a mixture of tris(trimethylsilyl)ketenimine (**1**) (80%) and tris(trimethylsilyl)ethynylamine (**9**) (20%). Ynamine **9** was isolated by preparative gc and characterized, Table III. Ketenimine **1** was obtained by heating the mixture of isomers at 160° to convert all of **9** to **1**. The ratio of **9** to **1** was increased to 1:1 by removing the ether, either by filtration or distillation, and replacing it with THF before adding trimethylchlorosilane at −78°.

1 showed the expected ir and nmr spectra, $n^{24}D$ 1.4546 (lit.[9] $n^{20}D$ 1.4560), λ_{max} in cyclohexane 225.5 (log ε 4.00) and 285 nm (log ε 0.88).

B. Propanenitrile. Dropwise addition of 1.0 ml (0.015 mol) of propanenitrile to 30 ml of 1.2 *M tert*-butyllithium in pentane at −78° gave a white solid. The mixture was heated slowly to reflux to give 0.3 g (0.005 mol) of isobutane. After quenching the reaction with 5 ml (0.04 mol) of trimethylchlorosilane in 50 ml of THF at −78°, an anhydrous work-up gave 2 g of liquid, bp 65–85° at 10 Torr. Gc analysis showed this material to be a mixture of 1-chloro-1,1,3,3,3-pentamethyldisilylmethylene ($Me_3SiCH_2SiMe_2Cl$),[20] methyltrimethylsilyl-*N*-trimethylsilylketenimine (**15**), and 1,1-dimethyl-3-trimethylsilyliminopentane (**14**), the ratio of the latter two compounds being *ca.* 1:10. Each compound was isolated by preparative gc. $Me_3SiCH_2SiMe_2Cl$ was identified by comparing its retention time and nmr and ir spectra with those of an authentic sample. Compounds **14** and **15** are characterized in Table III.

The ratio **15**:**14** was increased to 1:2 by complexing the *tert*-butyllithium with 1 equiv of TMEDA prior to addition of propanenitrile.

C. Isobutanenitrile. Isobutanenitrile (3.7 ml, 0.04 mol) in pentane (20 ml) was added to 50 ml of 1.2 *M tert*-butyllithium in pentane at −78°. Only a trace of isobutane was obtained when the solution was warmed to reflux. The reaction was quenched with 7.7 ml (0.06 mol) of trimethylchlorosilane in 20 ml of THF at −78°. Anhydrous work-up gave 6.5 g (82%) of 2,2,4-trimethyl-3-(trimethylsilylimino)pentane: bp 75–80° at 10 Torr; $n^{23}D$ 1.4300; ir (neat) ν (cm^{-1}) 1730 (C=N), 1250 (Me_3Si); nmr (CCl_4, TMS) τ 6.95 (septet, 1, CH), 8.97 and 9.08 (d and s, 15, CMe_2 and CMe_3), 9.85 (s, 9, Me_3Si).

Anal. Calcd for $C_{11}H_{25}NSi$: C, 66.3; H, 12.6; N, 7.0; Si, 14.1. Found: C, 66.16; H, 12.41; N, 7.29; Si, 13.85.

D. Trimethylsilylacetonitrile. Trimethylsilylacetonitrile (**3**) (2.4 ml, 0.018 mol) in 10 ml of hexane was added dropwise to 33 ml of 1.2 *M tert*-butyllithium in pentane. After heating the solution at reflux for 1 hr, 2.0 g (0.034 mol) of isobutane was obtained. Reaction was quenched by cooling it to −78° and adding 30 ml of THF and 6.3 ml (0.05 mol) of trimethylchlorosilane. Anhydrous work-up gave 4.6 g of a mixture of ketenimine (**1**) (80%) and ynamine (**9**) (20%).

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[20] This disilylmethylene is formed from the reaction of excess *tert*-butyllithium with trimethylchlorosilane.[18b]

E. **Bis(trimethylsilyl)acetonitrile.** Addition of 2 g (0.011 mol) of bis(trimethylsilyl)acetonitrile in 10 ml of hexane to 8 ml of 1.6 *M* *n*-butyllithium in hexane gave a white solid. Derivatization of the solid with 2 ml (0.015 mol) of trimethylchlorosilane in 10 ml of THF gave 2.5 g (90%) of **1**; no trace of **9** was detected.

Reactions of Dilithioacetonitrile. A. Acetaldehyde. Acetaldehyde (6.8 ml, 0.12 mol) was added to 0.037 mol of Li_2C_2HN, prepared as described in part A above, in ether at −78°. The mixture was stirred for 2 hr at −78° and 50 ml of THF and 15.5 ml (0.12 mol) of trimethylchlorosilane were added. The mixture was slowly warmed to and kept at reflux for 2 hr. Anhydrous work-up gave 0.5 g (10%) of 3-trimethylsiloxybutanenitrile (**6**), bp 50° at 0.3 Torr; 6.3 g (70%) of bis(1-trimethylsiloxyethyl)acetonitrile (**7**), bp 85–90° at 0.3 Torr; and 0.5 g (5%) of tris(1-trimethylsiloxyethyl)acetonitrile (**8**), bp 120° at 0.3 Torr. 3,3-Dimethyl-2-(trimethylsiloxy)butane (**16**), $Me_3SiOCHMeCMe_3$, bp 35–45° at 10 Torr, was also isolated. Characteristics of compounds **6**, **7**, **8**, and **16** are given in Table III.

B. **Acetone.** Acetone (5.5 ml, 0.075 mol) was added slowly to 0.018 mol of Li_2C_2HN in ether at −78°. After 1 hr the mixture was warmed to room temperature and 10 ml (0.075 mol) of trimethylchlorosilane was added. Anhydrous work-up gave 1.6 g (47%) of 2,4-bis(trimethylsiloxy)-2,4-dimethyl-3-cyanopentane, Table III.

C. **1-Bromobutane.** A solution of 53 ml (0.5 mol) of 1-bromobutane in 100 ml of THF was added to 0.1 mol of Li_2C_2HN in ether at −78°. After 2 hr the reaction was warmed to and kept at room temperature overnight. Water (100 ml) was added cautiously. The organic phase was dried with sodium sulfate and distilled to give 8 g (40%) of tri-*n*-butylacetonitrile, bp 125–130° at 5 Torr, $n^{25}D$ 1.4419 (lit.[21] bp 126–128° at 5 Torr, $n^{24}D$ 1.4390).

D. **Benzyl Chloride.** In a manner similar to the above 0.037 mol of Li_2C_2HN was quenched with 15 ml (0.13 mol) of benzyl chloride to give 3.2 g (30%) of tribenzylacetonitrile, mp 220–221° (lit.[22] mp 218–220°).

E. ***tert*-Butyldimethylchlorosilane.** A solution of 15 g (0.1 mol) of *tert*-butyldimethylchlorosilane[23] in 100 ml of THF was added to 0.25 mol of Li_2C_2HN in ether at −78°. Reaction was kept at −78° for 4 hr and then warmed to and kept at room temperature for 1 day. Anhydrous work-up gave 8 g (83%) of clear liquid, bp 95–125° at 0.5 Torr. Gc and nmr analysis showed tris(*tert*-butyldimethylsilyl)ethynylamine (**10**) and tris(*tert*-butyldimethylsilyl)ketenimine (**11**) to be present in the ratio 2:1. **10** was isolated by preparative gc, and **11** was obtained by heating the mixture of isomers in a sealed tube at 250° for 7 days (Table III). **11** showed two absorptions in the uv spectrum: λ_{max} in cyclohexane 232 (log ϵ 3.96) and 295 nm (log ϵ 0.91). Compounds **10** and **11** both showed P-Bu peaks at *m/e* 326 in the mass spectra, no parent peaks being detected.

F. **Dimethylchlorosilane.** A slurry of 0.022 mol of Li_2C_2HN in ether was added to a solution of 13 ml (0.12 mol) of dimethylchlorosilane in 75 ml of THF at −78°. The mixture was slowly warmed to 30° and stirred for 16 hr. Anhydrous work-up gave 3.9 g (80%) of clear liquid, bp 45–48° at 0.5 Torr. Gc analysis showed tris(dimethylsilyl)ethynylamine (**12**) and tris(dimethylsilyl)ketenimine (**13**) to be present in the ratio 1:2. **12** could not be separated from **13** by preparative gc. Because the SiH stretching absorption masks the C≡C stretching absorption in ir, **12** was identified in the crude product by nmr spectroscopy. Two doublets are observed at τ 9.68 (12, Me_2SiN) and 9.87 (6, Me_2SiC). These absorptions disappear when the sample is heated at 160° for 6 hr and only absorptions due to ketenimine **13** remain (Figure 1).

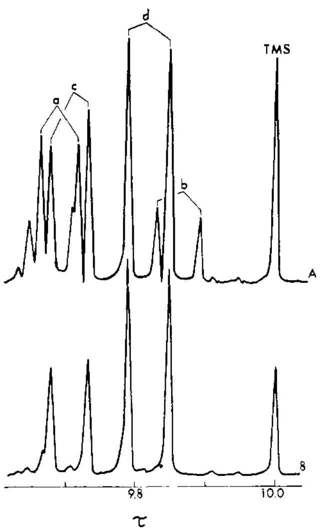
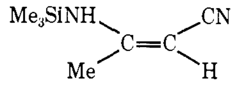


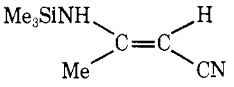
Figure 1. Dimethylsilyl region of proton nmr spectra of: (A) crude mixture of $(HMe_2{}^aSi)_2NC{\equiv}CSiMe_2{}^bH$ (**12**) and $HMe_2{}^cSiN{=}C{=}C(SiMe_2{}^dH)_2$ (**13**); (B) same material after 6 hr at 160°.

Ketenimine **13** was obtained by heating the above mixture of isomers at 160° for 6 hr (Table III).

3-Trimethylsilylaminocrotononitrile and 3-Trimethylsilylaminoisocrotononitrile. Acetonitrile (5.0 ml, 0.094 mol) in 25 ml of ether was added dropwise to a solution of 8.5 g (0.047 mol) of *N*-sodiohexamethyldisilazane[24] in 47 ml of ether at room temperature. After 5 hr, 6.6 ml (0.047 mol) of trimethylchlorosilane was added and the mixture was stirred overnight. Sodium chloride was filtered and the filtrate distilled rapidly on a 6-in. Vigreux column to give 1.6 g of 3-trimethylsilylaminocrotononitrile (**17**), bp 138–145° at 20



Torr, and 3.0 g of 3-trimethylsilylaminoisocrotononitrile (**18**),



bp 165–170° at 20 Torr. The lower boiling isomer was assigned the crotononitrile structure because intramolecular hydrogen bonding would be more favorable for this isomer.

17 was characterized as follows: ir (neat) ν (cm^{-1}) 3300 (NH), 2190 (CN), 1600 (C=C), 1250 (Me_3Si); nmr (CCl_4, TMS) τ 5.3 (s, 1, NH), 6.18 (s, 1, CH), 8.07 (s, 3, MeC), 9.72 (s, 9, Me_3Si); $n^{21}D$ 1.4895.

18 showed the following characteristics: ir (neat) ν (cm^{-1}) 3300 (NH), 2190 (CN), 1600 (C=C), 1250 (Me_3Si); nmr (CCl_4, TMS) τ 5.3 (s, 1, NH), 6.02 (s, 1, CH), 7.89 (s, 3, MeC), 9.75 (s, 9, Me_3Si); $n^{21}D$ 1.5039.

These properties are similar to those reported for 3-trimethylsilylaminocrotononitrile.[6]

Attempts to further purify each isomer by preparative gc gave mixtures of **17** and **18** (ratio 3:2).

Attempts to Prepare Trisilyl Ynamines. Addition of 1.3 ml (0.01 mol) of chloroethynyltrimethylsilane[25] to a solution of 2.2 g (0.011 mol) of *N*-sodiohexamethyldisilazane in 10 ml of hexamethylphosphoramide gave a black mixture. Anhydrous work-up gave 1.5 g (65%) of tris(trimethylsilyl)amine (**4**), bp 85° at 12 Torr, mp 72° (lit.[26] mp 70–71°). Ir spectrum and retention time on gc were identical with those of an authentic sample.

Chloroethynylbenzene[27] (2.5 g, 0.018 mol) was added to a solution of 7.0 g (0.019 mol) of *N*-sodiohexamethyldisilazane in 50 ml of THF. Anhydrous work-up after 3 days gave 2.2 g (55%) of trisilylamine **4**, identified in the same manner described above.

Metalation of Acetonitrile with *N*-Sodiohexamethyldisilazane. A solution of 1.1 ml (0.022 mol) of acetonitrile in 20 ml of ether was added dropwise to a solution of 12 g (0.066 mol) of *N*-sodiohexamethyldisilazane at −60°. Reaction was stirred at room temperature for 3 hr, then filtered in a nitrogen atmosphere. The filtrate was heated at reflux with 6 ml (0.045 mol) of trimethylchlorosilane for 16 hr. Anhydrous work-up gave 3.6 g (0.022 mol) of hexamethyldisilazane, 55–60° at 45 Torr, and 6.7 g (0.03 mol) of tris-

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(trimethylsilyl)amine (**4**). Both compounds were identified by comparison of gc retention times and ir spectra with those of authentic samples.

After the solid was slurried with 50 ml of ether, 3 ml (0.03 mol) of trimethylchlorosilane was added over a period of 1 min. The infrared spectrum of the crude product showed absorptions due to acetonitrile, trimethylsilylacetonitrile (**3**), bis(trimethylsilyl)acetonitrile (**2**), tris(trimethylsilyl)ketenimine (**1**), and an unidentified nitrile. Gc analysis indicated **1**, **2**, and **3** to be present in the ratio 6:1:3, respectively. No appreciable amount of expected trimethylsilyl acetonitrile dimers, **17** and **18**, were detected by gc.

In a second experiment the solid was slurried with 50 ml of ether and 3.6 g (0.022 mol) of benzophenone in 100 ml of ether was added. The mixture was stirred for 16 hr, then poured into a mixture of dilute dihydrochloric acid and ice. The organic phase was separated and concentrated. Recrystallization of the residue from 10 ml of 95% ethanol gave 3 g (60%) of 3,3-diphenyl-3-hydroxypropanenitrile, mp 138–140° (lit.[7] mp 141–143°).

Polylithium Compounds. V.[1,2] Polylithium Compounds from Phenylpropynes and Their Polysilicon Derivatives

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Abstract: The species $C_9Li_6H_2$ and $C_9Li_5H_3$ are the major products formed when 1-phenylpropyne is heated with 50 equiv of *n*-butyllithium. Lesser amounts of C_9Li_7H, $C_9Li_4H_4$, $C_9Li_3H_3$, and possibly a trace of the perlithio compound C_9Li_8 are formed also. Derivatization of the reaction mixture with deuterium oxide gives a mixture of deuterated 3- and 1-phenylpropynes. Nine new trimethylsilylphenylallenes and -propynes were prepared by derivatizing the lithiated phenylpropynes and -allenes with trimethylchlorosilane. The structures of several polylithium compounds were studied by infrared spectroscopy.

Many polylithium compounds have been prepared recently by metalation using alkyllithium compounds. Terminal acetylenes and *n*- or *tert*-butyllithium give C_3Li_4,[3,4] C_5Li_4,[5] RC_3Li_3 (R being hydrogen, methyl, propyl, or pentyl),[3,4] and several dilithium compounds.[3,4,6] Klein and coworkers have prepared several dilithium compounds, which they call sesquiacetylides, by treating various enynes[7] and internal acetylenes[8] with *n*-butyllithium. Toluene and *n*-butyllithium-*N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA) give di- and trilithiotoluenes.[9] Acetonitrile and *tert*-butyllithium give Li_2C_2HN.[2] Mulvaney, Folk, and Newton[10] have described the formation of C_6H_5-C_3Li_3 and $C_6H_4LiC_3Li_3$ from 1-phenylpropyne and *n*-butyllithium in refluxing hexane.

This latter work is of interest for two reasons. It represents the first example of polylithiation of a nonterminal acetylene. Second, it is surprising how easily the phenyl ring in this compound is metalated (toluene is not metalated by *n*-butyllithium in refluxing hexane). The fact that four hydrogens of 1-phenylpropyne can be replaced by lithium atoms under these relatively mild conditions suggested that metalation under more stringent conditions might give highly lithiated compounds having unusual structures and properties.

Results and Discussion

Distillation of solvent from a solution of 1-phenylpropyne and 50 equiv of *n*-butyllithium in hexane gives a bright red oil, which upon heating at 75–85° gradually forms a reddish brown slurry, and finally solidifies into a black solid. This solid readily forms a slurry with anhydrous hexane. Slow addition of deuterium oxide to this slurry gives a mixture of deuterated 3- and 1-phenylpropynes in *ca.* 60% yield, both isomers being present in approximately equal amounts. Analysis of these propynes by mass spectroscopy (Table I, run 5) shows the major products to be $C_9D_6H_2$ and $C_9D_5H_3$ along with lesser amounts of C_9D_7H, $C_9D_4H_4$, $C_9D_3H_5$, and even a trace of C_9D_6!

Derivatizing the slurry obtained from treating 1-phenylpropyne with 30 equiv of *n*-butyllithium with trimethylchlorosilane in THF at 0° gives a mixture of tri-, tetra-, and pentasilylated products (1:2.5:3) as shown.

$$C_9H_6 + 30n\text{-BuLi} \longrightarrow \xrightarrow{Me_3SiCl} C_9H_5(SiMe)_3 + C_9H_4(SiMe_3)_4 + C_9H_3(SiMe_3)_5$$

Although they may have been formed, no compounds containing more than five silicons were isolated from the residue. However, the tri-, tetra-, and pentasilyl derivatives accounted for only 60% of the starting material.

Several new compounds were isolated from this mixture by preparative gas chromatography. Only one trisilyl derivative, phenyltris(trimethylsilyl)allene, was obtained. Two tetrasilylated isomers were isolated in about equal amounts. Several pentasilyl isomers were formed but only one was obtained pure.

The structures of these isomers were assigned from their nmr spectra and by analogy with results obtained in polylithiation of toluene.[9] The high negative charge present in benzyllithium appears to change the mech-

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