TMEDA or HMPA shifts the infrared absorptions of lithiated acetylenes to much higher frequencies. This is also true for our compounds. The new absorptions appear at 1955 cm^{-1} for C_3Li_4, 1950 cm^{-1} for MeC_3Li_3, and 1910 and 2050 cm^{-1} for $Me_2C_3Li_2$, respectively. Possible explanations for this shift to higher frequency include (1) a change in aggregate structure, (2) a bond reorganization to a different structure, and (3) a change from tight ion pairs to solvent separated carbon–lithium bond.

(31) J. Klein and J. Y. Becker, *J. Chem. Soc., Chem. Commun.*, 576 (1973).

(32) D. Ballard and H. Gilman, *J. Organomet. Chem.*, **14**, 87 (1968).

(33) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds", Vol. 1, 3d ed, Methuen, London, 1967, p 31.

(34) R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Am. Chem. Soc.*, **83**, 4385 (1961).

(35) L. I. Smith and R. E. Kelley, *J. Am. Chem. Soc.*, **74**, 3305 (1952).

(36) K. N. Campbell and L. T. Eby, *J. Am. Chem. Soc.*, **62**, 1798 (1940).

(37) R. Ya. Levina, V. R. Skvarchenko, M. G. Kuz'min, and E. G. Treshchova, *Zh. Obshch. Khim.*, **26**, 2195 (1956).

(38) P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg, and F. L. Howard, *J. Res. Natl. Bur. Stand.*, **52**, 51 (1954).

(39) A. A. Petrov, B. S. Kupin, T. V. Yakovleva, and K. S. Mingaleva, *Zh. Obshch. Khim.*, **29**, 3732 (1959).

(40) C. C. Price and T. F. McKeon, *J. Polym. Sci.*, **41**, 445 (1959).

(41) H. M. Schmidt and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **86**, 1138 (1967).

Polylithium Compounds. 9.[1] Sequential Derivatizations of C_3Li_4, MeC_3Li_3, and $Me_2C_3Li_2$ with Diethyl Sulfate and Trimethylchlorosilane

Witta Priester and Robert West*

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received December 12, 1975

Abstract: Silylation of C_3Li_4 with trimethylchlorosilane is very slow in THF at 0 °C. Reaction of C_3Li_4 with a tenfold excess of both trimethylchlorosilane and diethyl sulfate resulted in formation of the triethylated, monosilylated derivative, $Et_3C-C\equiv C-SiMe_3$ as the major product. Derivatization of C_3Li_4, MeC_3Li_3, and $Me_2C_3Li_2$ with diethyl sulfate and trimethylchlorosilane in various orders of addition have been studied, and the results are explained in terms of the hard–soft acid–base theory.

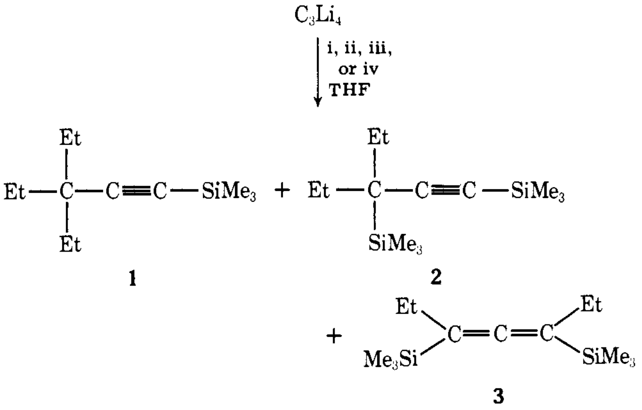
Introduction

In the previous paper we reported the polymetalation of propyne, 1- and 2-butyne, and 3-methylbutyne to give C_3Li_4, MeC_3Li_3, and $Me_2C_3Li_2$.[1,2] These lithiated hydrocarbons give modest to good yields of acetylenes and allenes when derivatized with alkyl sulfates, chlorosilanes, and chlorogermanes. With C_3Li_4, the reaction proceeds through the intermediates RC_3Li_3 and the dilithiopropargylide, $[R_2\text{-}C{\overset{-}{=}}C{\equiv}C\text{-}Li]Li$. Derivatization of the latter intermediate determines the acetylene to allene ratio. Reaction at the propargylic position occurs with small derivatizing agents to give acetylenic products, whereas derivatization at carbon atom 1 occurs with large derivatizing agents to give allenic products. In this paper, we report our results on sequential derivatization of C_3Li_4, MeC_3Li_3, and $Me_2C_3Li_2$.

Results

Tetralithiopropyne was reacted at 0 °C in THF–hexane with 2 equiv trimethylchlorosilane (TMCS) for 3 h, followed by addition of excess diethyl sulfate (DeS). Three products, **1**, **2**, and **3**, were formed in a 10:1:1 ratio. Surprisingly, the major product was the triethylmonosilyl derivative **1**. The same products in the same ratio were obtained (a) when C_3Li_4 was derivatized at 0 °C with 3 equiv of TMCS, followed 2 h later with DeS; (b) when C_3Li_4 was added dropwise to a mixture of 10 equiv of both DeS and TMCS; and (c) when 2 equiv of DeS was first added, followed 2 h later by 2 equiv of TMCS (see Scheme I).

Scheme I



rel ratio **1**:**2**:**3** is 10:1:1

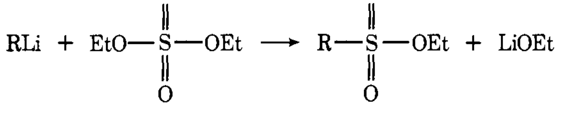
i. 2 equiv $SiMe_3Cl$, 2 h, 0 °C, followed by 2 equiv Et_2SO_4
ii. 3 equiv $SiMe_3Cl$, 2 h, 0 °C, followed by 2 equiv Et_2SO_4
iii. 2 equiv Et_2SO_4, 2 h, 0 °C, followed by 2 equiv $SiMe_3Cl$
iv. added to 10 equiv Et_2SO_4 and 10 equiv $SiMe_3Cl$

Formation of **1** might have resulted from initial derivatization with only 1 equiv of TMCS to give **4**, followed by ethylation of this trianion. However, when 1-trimethylsilyl propyne was trilithiated and derivatized with 1 equiv of TMCS followed by addition of excess DeS, five products were formed in approximately equal amounts. This is very different from the 10:1:1 product distribution from C_3Li_4 under these conditions and eliminates **4** as the intermediate in the formation of **1** from C_3Li_4.

$$[Me_3Si-C\equiv C\equiv C]^{-3}$$

4

Another possibility was that **1** might have resulted from a more highly silylated precursor. It is known that ethoxide ion can be produced by reaction of organolithium reagents at the sulfur of diethyl sulfate.[3] Attack of lithium ethoxide at the



$$RLi + EtO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OEt \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OEt + LiOEt$$

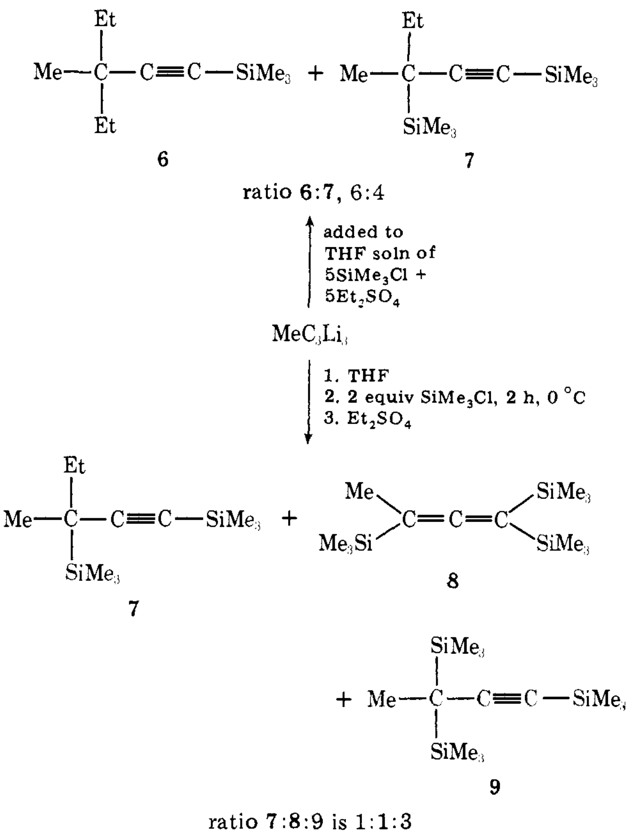
silicon of a disilylated intermediate might then have produced a monosilylated precursor to **1**. However when 1,3-bis(trimethylsilyl)propyne was prepared,[4] dilithiated, and reacted with DeS, a 1:1 mixture of **2** and **3** was obtained. No triethylated products were formed, indicating that trimethylsilyl groups are not readily displaced from dianion **5**.

$$[\mathrm{Me_3Si{-}C{\equiv}C{\equiv}C{-}SiMe_3}]^{-2}$$

5

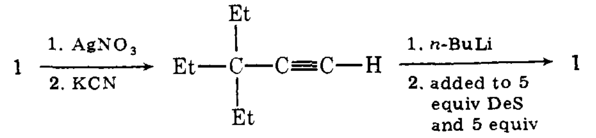
In order to probe the course of these reactions, several experiments utilizing less highly lithiated intermediates were performed. Trilithio-1-butyne, MeC_3Li_3, was prepared and added to a THF solution containing 5 equiv of both DeS and TMCS. Two products were isolated, **6** and **7** (Scheme II). In another experiment derivatization of MeC_3Li_3 with 2 equiv of TMCS at 0 °C followed 2 h later by DeS gave a different product mixture containing the two tris(trimethylsilyl) derivatives **8** and **9** as the major products, with a small amount of the monoethyldisilyl product **7**.

Scheme II



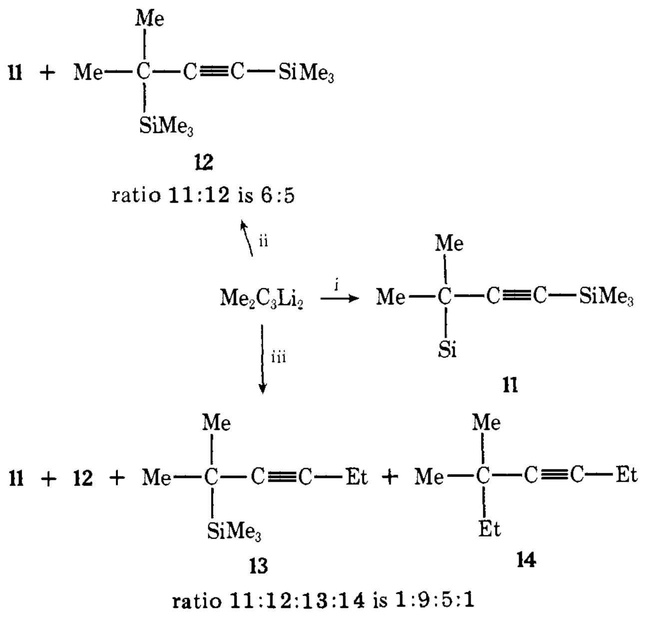
Similar experiments were performed on dilithio-3-methylbutyne, $Me_2C_3Li_2$ and are summarized in Scheme III. Here again the results depended on the order of addition of TMCS and DeS.

The relative rates of reaction for two simple anions with DeS and TMCS were also determined. The acetylide anion from 3,3-diethyl-1-pentyne (**10**) was prepared by hydrolysis of **1**[5] and lithiation with *n*-butyllithium. Addition of this anion to a THF solution containing 5 equiv of both DeS and TMCS resulted in exclusive silylation to give **1**. Similarly, addition of 1-lithiohexane to a THF solution containing a fivefold excess of both reagents gave only one product, 1-trimethylsilylhexane. No octane was formed.



10

Scheme III



i. 1 equiv Et_2SO_4, 2 h, 0 °C, followed by 1 equiv $SiMe_3Cl$
ii. added to $5SiMe_3Cl$ + $5Et_2SO_4$
iii. 1 equiv $SiMe_3Cl$, 2 h, 0 °C, followed by 1 equiv Et_2SO_4

Discussion

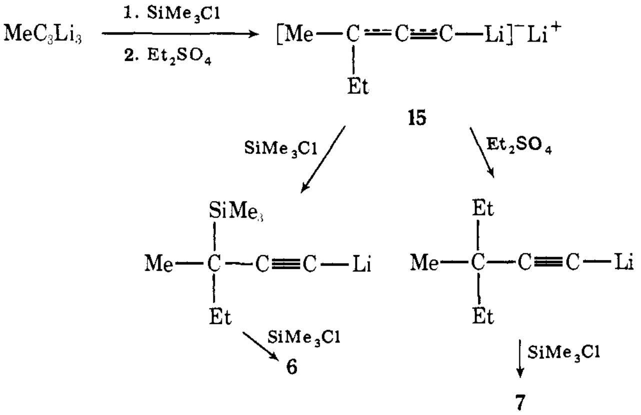
These results can best be explained utilizing Pearson's[6] hard-soft acid-base (HSAB) model. This model proposes that hard-hard (nonpolarizable-nonpolarizable) and soft-soft (polarizable-polarizable) interactions are favored over hard-soft interactions. Our polyanions have both hard and soft derivatization sites. The propargylic site having high p character can be characterized as soft while the acetylide site (sp hybridization) can be designated hard. Both DeS and TMCS are generally classified as hard,[7] but it is clear from our results that DeS must be significantly softer (vide infra). Addition of 1-hexyllithium and 1-lithio-3,3-diethylpentyne to excess DeS and TMCS results in exclusive silylation, indicating that both these anions are hard enough to prefer reaction with the harder TMCS.

Reaction of $Me_2C_3Li_2$ with 1 equiv of DeS followed by 1 equiv of TMCS gives exclusive ethylation at the soft propargylic site and subsequent silylation of the resulting hard acetylide anion. However, the two methyl groups of $Me_2C_3Li_2$ make the propargyl position hard enough so that some silylation does occur when both DeS and TMCS are present. Therefore addition of $Me_2C_3Li_2$ to 5 equiv of both DeS and TMCS gives products which indicate that ethylation and silylation of this propargylic anion are competitive, although ethylation is marginally preferred. Exclusive silylation of the resulting acetylide anion then occurs. Reaction of $Me_2C_3Li_2$ with 1 equiv of TMCS at 0 °C for 2 h results in silylation of the propargyl site, and in fact this reaction is competitive with silylation of the acetylide; that is, not all the acetylide formed is silylated. Upon addition of DeS the resultant anion mixture eventually ethylates.

Our results indicate that C_3Li_4 is much more selective in these derivatization reactions than dilithiopropargylides. This very soft anion does not react with TMCS at 0 °C in 2 h! However, upon addition of the softer Lewis acid DeS, ethylation does occur. The resulting triethylated acetylide then reacts with TMCS to form product **1**. In this case the order of addition of the reagents is unimportant since reaction with TMCS is so slow. The same product mixture resulted regardless of how the reaction was performed (Scheme I).

The propargyl position of MeC_3Li_3 is intermediate in hardness between $Me_2C_3Li_2$ and C_3Li_4. It is clear that MeC_3Li_3 is not as soft or selective as C_3Li_4, for when MeC_3Li_3 is reacted with 2 equiv of TMCS silylation does take place. The major products are the tris(trimethylsilyl)allene and acetylene, **8** and **9**. The increased hardness of the propargyl position, which is due to the methyl group of MeC_3Li_3, increases the rate of reaction with TMCS at this site. On the other hand, the products from addition of MeC_3Li_3 to a fivefold excess of both DeS and TMCS indicate that initial monoethylation of the propargyl position occurs (see Scheme **IV**). The resulting dilithiopropargylide, **15**, now having two alkyl groups at the propargylic site (as with $Me_2C_3Li_2$), shows only a slight preference for ethylation over silylation at the remaining propargyl position.

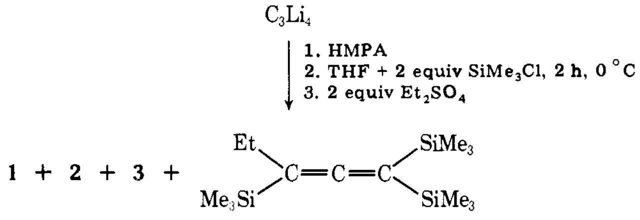
Scheme IV



Additional Experiments on C_3Li_4

In order to change the character of the anions present, the polar coordinating solvent hexamethylphosphoric triamide (HMPA) was added. Treatment of a HMPA solution of C_3Li_4 with 2 equiv of TMCS at 0 °C followed 2 h later by DeS gave four products, **1**, **2**, **3**, and **16** in ratios of 3:1:1:2 (see Scheme V). As expected, the HMPA increased the hardness of the anions present and some silylation occurred. Formation of mono-, di-, and trisilylated products indicates that in HMPA the rates of reaction for the first, second, and third carbon-lithium bonds are approximately the same (as are the acidities of the corresponding hydrogens in propyne),[3] and selective derivatization is not possible in this solvent.

Scheme V

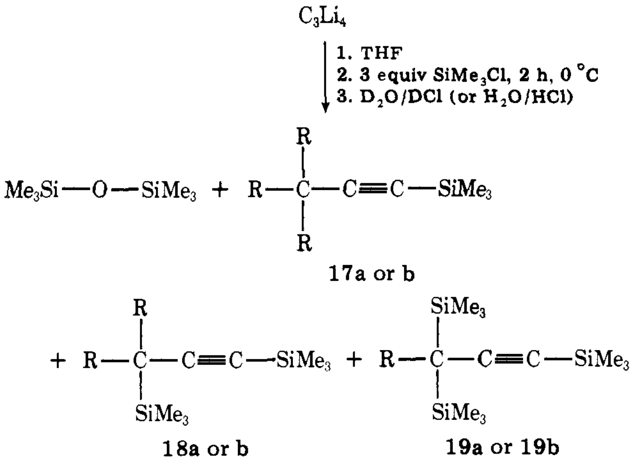


16

ratio **1**:**2**:**3**:**16** is 3:1:1:2

In another experiment, a THF solution of C_3Li_4 was reacted at 0 °C with 3 equiv of TMCS, followed 2 h later by quenching with D_2O/DCl (or H_2O/HCl) (see Scheme VI). It is interesting that the major product here, the monosilylated derivative **17**, is analogous to that obtained from reaction of C_3Li_4 with TMCS and DeS. However, it is known that deuterium (and proton) shifts can occur in these systems,[8] so these results cannot be used as a good indicator for the order of derivatization or the structure of the anions present.

Scheme VI

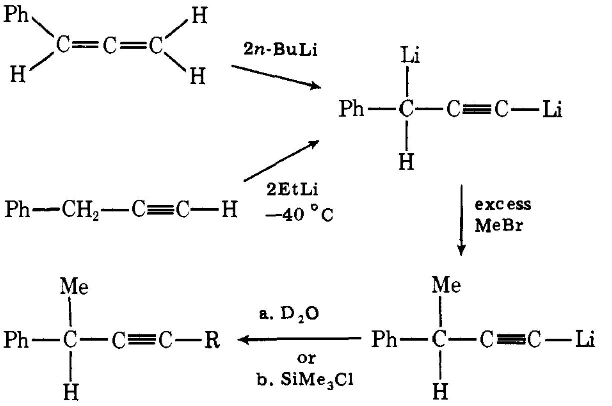


a, R = D
b, R = H

ratio **17**:**18**:**19** is 11:2:5

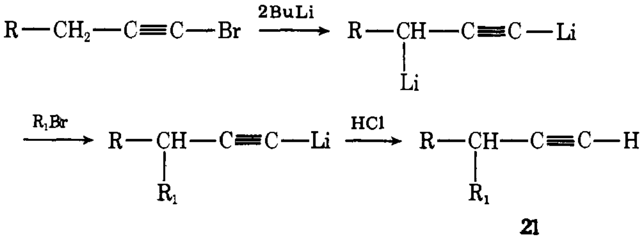
Literature Results

The HSAB model also explains several results on dilithiopropargylides that can be found in the chemical literature. For example, Brandsma and Mugge[9] found that a dianion is formed when phenylallene is metalated with 2 equiv of ethyllithium at −40 °C. Addition of excess methyl bromide followed by deuterolysis (D_2O) or quenching with TMCS resulted in acetylenic compounds **20a** and **20b**. Klein and Brenner[8] prepared the same dilithiated intermediate from 3-phenylpropyne and obtained identical derivatization results. Also, Scheinmann and co-workers[10] recently reported that 1-bromoalkynes can be dilithiated. Reaction of these intermediates with alkyl bromides followed by proteolysis (HCl) resulted in propargyl-substituted acetylenes **21**.



20

a, R = D
b, R = $SiMe_3$



21

R = Et, Pr, Bu, C_5H_{11}
R_1 = Et, Pr, Bu

These results make it clear that dilithiopropargylides can be selectively derivatized with soft derivatizing agents, i.e., alkyl bromides, at the soft propargyl position. The hard acetylide anion does not react with these soft reagents. However, the resulting monolithioacetylides can be silylated or protonated with the hard reagents, H_2O or TMCS.[11]

Experimental Section

General Procedures. All reactions involving organolithium compounds were carried out in an atmosphere of dry nitrogen. Hydrocarbon and ether solvents were freshly distilled from Na:K alloy before use. HMPA was distilled under reduced pressure from calcium hydride. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Gas chromatographic analyses and separations were made on a Barber-Colman Model 5430 thermal conductivity gas chromatograph. The following columns were used: (a) 15 ft × ¼ in. 20% SE 30 on Chromosorb W; (b) 15 ft × ¼ in. 20% QF-1 on Chromosorb W; (c) 15 ft × ¼ in. 20% Carbowax 20M on Chromosorb W.

n-Butyllithium in hexane was obtained from Foote Mineral Co. Trimethylchlorosilane, Dow Corning Corp., was distilled before use. Diethyl sulfate, Aldrich Gold Label, was stirred over anhydrous sodium carbonate until neutral to Congo red paper, distilled, and then stored over KOH. D_2O was purchased from Columbia Organic Chemicals.

Spectra were recorded by means of the following instruments: infrared, Perkin-Elmer 457, Beckman ir 33; ^1H NMR, Varian A-60A, JEOL MH-100, ^{13}C NMR, JEOL FX-60; mass spectra, AEI-MS 902 at 70 eV.

Sequential Derivatizations of C_3Li_4 in THF. a. TMCS (2 equiv) followed by 2 equiv of DeS. To a solution prepared by addition of 80 mmol of propyne to 320 mmol of *n*-butyllithium was added 50 ml of diethyl ether and 50 ml of THF at 0 °C. Trimethylchlorosilane (17.4 g, 160 mmol) was added dropwise and stirred for 2 h. The resulting mixture was cooled to −78 °C, and 26 g (170 mmol, 19 ml) of DeS was added. After warming to room temperature and stirring for 16 h, the mixture was hydrolyzed, extracted, dried ($MgSO_4$), and rotary evaporated. Distillation then yielded 7.1 g of product, bp 25–48 °C (150 μm). It was estimated by GLC (column a, 170 °C) that 5.0 g (70% of total area) of compound **1** was present (32% yield) and that 1.1 g (15% of total area) of a mixture of **2** and **3** was present (6% yield for each). The following spectral data were observed.

5,5-Diethyl-2,2-dimethyl-2-sila-3-heptyne (3,3-Diethyl-1-trimethylsilyl-1-pentyne, 1). ^1H NMR (CCl_4) δ 0.015 (s, 9 H), 0.92 (m, 9 H), 1.47 (m, 6 H); IR (CCl_4) 2162, 2140, 1245, 960, 850, 835 cm^{-1}; mass spectrum *m/e* (rel intensity) 197 (4), 196 (15), 181 (28), 167 (38), 111 (18), 97 (62), 73 (100). Anal. Calcd for $C_{12}H_{24}Si$: C, 73.37; H, 12.33. Found: C, 73.32; H, 12.21.

The GC retention time, NMR, and IR for **2** and **3** were similar to that prepared from lithiation and ethylation of 1,3-bis(trimethylsilyl)propyne. The proton-decoupled ^{13}C NMR spectrum of **3** in deuteriobenzene using $Cr(acac)_3$ as a relaxation agent confirms the assigned structure. The spectrum consists of singlets at 205.4 ppm relative to Me_4Si, $>C{=}\mathit{C}{=}C<$; 91.9, $>\mathit{C}{=}C{=}\mathit{C}<$; 22.2, $CH_3\text{–}\mathit{C}H_2\text{–}$; 14.3, $\mathit{C}H_3\text{–}CH_2\text{–}$; −1.1, $Si\text{–}(\mathit{C}H_3)_3$.

b. TMCS (3 equiv) followed by 2 equiv of DeS. In a manner similar to that described above, a THF solution of C_3Li_4 was reacted with 3 equiv of TMCS at 0 °C for 2 h, followed by addition of 2 equiv of DeS. After workup, GLC analysis showed an identical product distribution with that described above.

c. DeS (2 equiv) followed by 2 equiv of TMCS. In a similar manner to a above, C_3Li_4 was reacted in THF with 2 equiv of DeS at 0 °C; after 2 h, 2 equiv of TMCS was added. GLC of the resultant product mixture showed an identical product distribution with a above.

d. Addition of C_3Li_4 to 10 equiv of DeS and 10 equiv of TMCS. A solution of C_3Li_4 was added dropwise to a mixture of THF, 10 equiv of DeS, and 10 equiv of TMCS at 0 °C. The red C_3Li_4 color disappeared upon addition. After 16 h at room temperature the solution was hydrolyzed, extracted, dried ($MgSO_4$), rotary evaporated, and Kugelrohr distilled. GLC analysis of the distillate showed an identical product distribution with that described above except for a residual peak due to DeS. The DeS could be removed by refluxing the product mixture with a 20% alcoholic KOH solution for 1 h.

Derivatization of C_3Li_4 with TMCS Followed by DeS in the Presence of HMPA. To a solution prepared by lithiating 80 mmol of propyne with 320 mmol of *n*-butyllithium was added 30 ml of HMPA and 100 ml of THF. To this mixture at 0 °C was added 160 mmol of TMCS (17.3 g, 20.4 ml), followed 2 h later by 160 mmol of DeS (24.6 g, 21.0 ml). After warming to room temperature, the solution was heated at reflux for 3 h. The mixture was then hydrolyzed, extracted, dried ($MgSO_4$), rotary evaporated, and Kugelrohr distilled, yielding 6.5 g of products, bp 25–75 °C (100 μm). These were separated by GLC on column a (185 °C) into three components: **1**, (43% of total area), **2** and **3** (1:1 mixture, 31%), and **16** (27%); retention times 3.8, 6.4, and 10.4 min, respectively.

The spectral characteristics for 1,1,3-tris(trimethylsilyl)-1,2-pentadiene (**16**) were the following: ^1H NMR (CCl_4) δ 1.87 (q, J = 7.2 Hz, 2 H), 1.02 (t, J = 7.2 Hz, 3 H), 0.04 (s, 18 H), 0.00 (s, 9 H); IR (neat) 2965, 2905, 1890, 1260, 920, 850 cm^{-1}; mass spectrum *m/e* (rel intensity) 286 (10.5), 285 (21.6), 284 (M^+, 66), 370 (9.5), 269 (3), 211 (9.6), 198 (10), 197 (24), 196 (100), 183 (3.8), 182 (9), 181 (40), 157 (3.2), 156 (5.6), 155 (29), 141 (9.4), 125 (2.4), 124 (2.4), 123 (14), 122 (40), 100 (1.4), 99 (11.4), 97 (9.2), 83 (8.2); exact mass, 284.1829 (calcd for $C_{14}H_{32}Si_3$: 284.1812).

Derivatization of C_3Li_4 with 3 Equiv of TMCS Followed by D_2O (or H_2O). A hexane solution of C_3Li_4 was prepared from 40 mmol of propyne and 160 mmol of *n*-butyllithium. The hexane was removed by vacuum and 100 ml of dry freshly distilled pentane plus 50 ml of THF was added. TMCS (15.3 ml, 120 mmol) was added at 0 °C and allowed to stir for 2.5 h. Five grams 10% DCl in D_2O was added followed by 50 ml of H_2O. The organic phase was separated, washed with three portions H_2O, and dried ($MgSO_4$). Distillation yielded 5.3 g of product, bp 95–105 °C at 760 Torr, and a residue which was vacuum distilled to give 2.6 g of product, bp 25–80 °C (150 μm). The low-boiling fraction was analyzed by GLC (column c, 70 °C) and shown to contain mostly dimethylsiloxane and **17** (ratio 3:2, yield of **17**, 43%). Gas chromatography of the higher boiling fraction indicated that approximately 1.2 g (55% of total area) of compound **18** was present (16% yield) and that approximately 0.6 g (22% of total area) of compound **19** was present (6% yield). Similarly reaction with HCl, H_2O was performed. GC retention times were identical for the hydrogen and deuterium derivatives.

Spectral data for the deuterio derivatives follows.

3,3,3-Trideuterio-1-trimethylsilylpropyne (17a). ^1H NMR (CCl_4) singlet at δ 0.07; IR (neat) 2970, 2910, 2200 (s), 1255 (s), 1135, 1050, 850, 770 cm^{-1}; mass spectrum *m/e* (rel intensity) 116 (1.1), 115 (9.3), 101 (10.7), 100 (100), 99 (7.0), 70 (8.0), 43 (7.9); exact mass, 115.0893 (calcd for $C_6H_9D_3Si$: 115.0897).

3,3-Dideuterio-1,3-bis(trimethylsilyl)propyne (18a). ^1H NMR (CCl_4) δ 0.11 (s); IR (neat) 2960, 2900, 2170, 1410, 1255, 1000, 910, 770, 710, 650 cm^{-1}; mass spectrum *m/e* (rel intensity) 187 (3), 186 (19), 172 (6), 171 (32), 98 (23), 74 (8), 73 (100); exact mass, 181228 (calcd for $C_9H_{18}D_2Si_2$: 186.1229).

3-Deuterio-1,3,3-tris(trimethylsilyl)propyne (19a). ^1H NMR (CCl_4) δ 0.10 (s); IR (neat) 2960, 2900, 2200, 2160, 2140, 1410, 1255, 895, 850, 770, 700, 650 cm^{-1}; mass spectrum *m/e* (rel intensity) 257 (13), 242 (22), 169 (40), 168 (15), 155 (15), 154 (11), 73 (100); exact mass, 257.1561 (calcd for $C_{12}H_{27}DSi_3$: 257.1562).

Metalation and Ethylation of 1,3-Bis(trimethylsilyl)propyne. To 0.2 g (6.5 mmol) of 1,3-bis(trimethylsilyl)propyne[4] in 20 ml of diethyl ether at 0 °C was added 10 ml of 1.6 M *n*-butyllithium (16 mmol). The solution was refluxed for 2 h, then 2.0 g (13 mmol) of Et_2SO_4 was added at 0 °C, and stirring was continued for 16 h. Water (30 ml) was added; the mixture was extracted with ether and dried over $MgSO_4$. Kugelrohr distillation yielded 1.0 g (54%) of diethylated products [bp 25–55 °C (100 μm)]. Separation of the two isomers was effected on column c (115 °C), retention time 7.1 and 8.5 min for the allene **3** and acetylene **2**, respectively (peak ratio 9:11). The spectral data were the following.

2,2,6,6-Tetramethyl-5,5-diethyl-2,6-disila-3-heptyne (2). ^1H NMR (CCl_4) δ 1.50 (q, J = 7 Hz, 4 H), 0.91 (t, J = 7 Hz, 6 H), 0.10 (s, 9 H), 0.08 (s, 9 H); IR (neat) 2970, 2177, 2150, 1260, 855 cm^{-1}; mass spectrum *m/e* (rel intensity) 241 (6), 240 (25), 225 (4), 155 (42), 153 (16), 152 (100), 151 (13), 137 (43), 123 (9), 97 (9), 83 (8); exact mass, 240.1728 (calcd for $C_{13}H_{28}Si_2$: 240.1729).

3,5-Bis(trimethylsilyl)-3,4-heptadiene (3). ^1H NMR (CCl_4) δ 1.85 (q, J = 7 Hz, 4 H), 0.96 (t, J = 7 Hz, 6 H), 0.03 (s, 18 H); ^{13}C NMR (C_6D_6) ppm relative to Me_4Si 205.4, 91.9, 22.5, 14.3, −1.1; IR (neat) 2960, 1900, 1850, 850 cm^{-1}; mass spectrum *m/e* (rel intensity) 240 (14), 225 (5), 211 (13), 167 (31), 152 (23), 137 (10), 123 (7), 111

(17), 99 (10), 73 (100); exact mass, 240.1728 (calcd for $C_{13}H_{28}Si_2$: 240.1729).

Hydrolysis of 1-Trimethylsilyl-3,3-diethyl-1-pentyne (1). The silylated acetylene **1** was only slowly hydrolyzed by refluxing in 20% ethanolic KOH, therefore the procedure of Schmidt and Arens[5] was used. To 1.96 g (10 mmol) of **1** in 30 ml of ethanol was added dropwise 5.0 g (30 mmol) of $AgNO_3$ dissolved in 10 ml of H_2O and 30 ml of EtOH. The solution turned orange, then dark. After 30 min, 9 g of KCN in 12.5 ml of H_2O was added dropwise. A voluminous precipitate formed. The mixture was stirred for 6 h, extracted with pentane, dried ($MgSO_4$), and the solvents were distilled. Kugelrohr distillation resulted in 0.9 g of product (75%), bp 30–75 °C (50 Torr). An analytically pure sample was obtained by preparative GLC (column b, 105 °C), retention time 2.2 min. The following spectral characteristics were observed.

3,3-Diethyl-1-pentyne (10).[12] ^{1}H NMR (CCl_4) δ 1.86 (s, 1 H), 1.38 (q, J = 7.5 Hz, 6 H), 0.85 (t, J = 7.5 Hz, 9 H); IR (neat) 3300, 2960, 2930, 2880, 2120, 2100, 1460, 1375, 915, 850, 630 cm^{-1}.

Lithiation and Derivatization of 3,3-Diethylpentyne. To 248 mg (2.0 mmol) of 3,3-diethylpentyne was added 1.25 ml of *n*-butyllithium (2.4 mmol). After 6 h, this solution was added to a mixture of 10 ml of THF, 1.27 ml of TMCS (10 mmol), and 1.3 ml of DeS (10 mmol) and stirred for 16 h. Water (10 ml) and 20 ml of hexane were added. The organic layer was washed with water, dried ($MgSO_4$), rotary evaporated, and Kugelrohr distilled to give 250 mg of product, bp 20–40 °C (150 μm). GLC (column a, 180 °C) indicated no octane was present. Preparative GLC gave an analytically pue sample which was shown by ^{1}H NMR and IR to be identical with an authentic sample of **1**.

Preparation and Derivatization of Hexyllithium. To 280 mg of lithium wire (0.04 g-atom) in 10 ml of hexane was added 2.4 g (20 mmol) of *n*-hexyl chloride dropwise. After 6 h reflux the resulting purple solution was added to a mixture of 15 ml of THF, 12.7 ml of TMCS (100 mmol), and 13 g (100 mmol) of DeS. Hydrolysis (H_2O), drying ($MgSO_4$), rotary evaporation, and Kugelrohr distillation resulted in 4.0 g of product, bp 25–30 °C (250 μ) (dry ice trap). Preparative GLC indicated that the product was a mixture of *n*-hexyl chloride and 1-trimethylsilylhexane.[13]

Derivatizations of $Me_2C_3Li_2$ with TMCS and DeS. a. DeS (1 equiv) followed by 1 equiv of TMCS. To a solution of $Me_2C_3Li_2$ prepared from 35 mmol of 3-methylbutyne at 0 °C was added 50 ml of THF and 5.4 g (35 mmol) of DeS. After 2 h 8.0 g (74 mmol) of TMCS was added, and stirring was continued for 30 h. The resulting mixture was hydrolyzed, extracted with hexane, dried ($MgSO_4$), and rotary evaporated resulting in 5.2 g of product. GLC analysis (column a, 130 °C) indicated that the only product formed was **11** (retention time, 4.6 min). The following spectral characteristics were observed.

1-Trimethylsilyl-3,3-dimethylpentyne (11). ^{1}H NMR (CCl_4) 1.41 (m, 2 H), 1.12 (s, 6 H), 0.97 (m, 3 H), 0.08 (s, 9 H); IR (CCl_4) 2975, 2195 sh, 2170, 1250, 960, 900, 850 cm^{-1}; mass spectrum *m/e* (rel intensity) 169 (4), 168 (21), 155 (4), 154 (15), 153 (100), 139 (16), 123 (8), 111 (15), 109 (6), 98 (10), 97 (90), 83 (9), 78 (13), 73 (44); exact mass, 168.1334 (calcd for $C_{10}H_{20}Si$: 168.1334).

b. Added to 5 equiv of TMCS and 5 equiv of DeS. A sample of $Me_2C_3Li_2$ prepared from 10.5 mmol of 3-methylbutyne was added dropwise to a stirred solution of 9.1 g (53 mmol) of DeS and 5.7 g (53 mmol) of TMCS in 20 ml of THF. After stirring for 16 h, the solution was hydrolyzed. The organic phase was separated, extracted, dried ($MgSO_4$), and rotary evaporated, yielding 5.0 g of crude product. The major component was DeS which was readily removed by hydrolyzing with 20% alcohol KOH at reflux. GLC analysis (column a, 135 °C) of the resulting solution showed that 6:5 ratio of **11** to **12**[1] was present, retention times 4.6 and 9.1 min, respectively.

c. TMCS (1 equiv) followed by 1 equiv of DeS. To a solution of $Me_2C_3Li_2$ prepared from 35 mmol of 3-methylpropyne was added 50 ml of THF and 4.4 ml (35 mmol) of TMCS. After 2 h at 0 °C, 4.7 ml (35 mmol) of DeS was added. After 16 h at 25 °C, water and then hexane were added, the organic phase was separated, dried ($MgSO_4$), and rotary evaporated to give 6.5 g of crude reaction mixture. GLC analysis (column a, 130 °C) of the resultant mixture showed that 4% **14**,[1] 4% **11**, 38% **12**,[1] and 24% **13** were present, retention times 3.6, 4.8, 6.9, and 9.6 min, respectively.

The spectral characteristics for **13** follow.

5-Methyl-5-trimethylsilyl-3-hexyne (13). ^{1}H NMR (CCl_4) δ 2.1 (q, J = 7.5 Hz, 2 H), 1.1 (s, 3 H), 1.1 (t, J = 7.5 Hz, 3 H); IR (CCl_4) 2965, 2860, 2230(w), 1320, 1250, 850 cm^{-1}; mass spectrum *m/e* (rel intensity) 169 (2.5), 168 (15), 153 (7), 111 (23), 97 (5), 74 (11), 73 (100); exact mass, 168.1333 (calcd for $C_{10}H_{20}Si$: 168.1334).

Derivatization of MeC_3Li_3 with TMCS and DeS. a. Added to 5 equiv of TMCS and 5 equiv of DeS. A solution of MeC_3Li_3 prepared from 30 mmol of 1-butyne was added dropwise to 50 ml of THF containing 9.7 g (90 mmol) of TMCS and 14 g (90 mmol) of DeS at 0 °C. After 2 h stirring, the resulting mixture was hydrolyzed by refluxing for 2 h with 20% KOH in EtOH. Hexane was added, the organic layer was separated, dried ($MgSO_4$), rotary evaporated and Kugelrohr distilled to give 5.5 g of product, bp 25–60 °C (250 μm) (collected in a dry ice trap). Hydrolysis of the excess DeS was accomplished by refluxing with 40 ml of 20% KOH for 1 h. After extraction and redistillation, GLC analysis indicated that 80% of the distillate was a mixture of **6** and **7** (ratio 6:4). Final purification of the 2.0-g sample was accomplished by preparative GLC (column a, 145 °C), retention times 5.0 and 9.2 min, respectively. The following spectral data were observed.

3-Ethyl-3-methyl-1-trimethylsilylpentyne (6). ^{1}H NMR (CCl_4) δ 1.30 (m, 4 H), 0.98 (s, 3 H), 0.84 (broad t, 9 H); IR (neat) 2960, 2920, 2870, 2160, 1455, 1378, 1250, 933, 855 (b), 765 cm^{-1}; mass spectrum *m/e* (rel intensity) 183 (2), 182 (13), 168 (8), 167 (51), 153 (26), 123 (11), 111 (28), 108 (14), 98 (12), 97 (100), 83 (11), 74 (7), 73 (81), 69 (18); exact mass, 182.1491 (calcd. for $C_{11}H_{22}Si$: 182.1491).

3-Methyl-1,3-bis(trimethylsilyl)pentyne (7). ^{1}H NMR (CCl_4) δ 1.46 (m, 2 H), 1.09 (s, 3 H), 0.99 (broad t, 3 H), 0.07 (s, 9 H), 0.04 (s, 9 H); IR (neat) 2950, 2140, 1248, 865 sh, 842, 760, 700 cm^{-1}; mass spectrum *m/e* (rel intensity) 227 (3), 226 (14), 155 (25), 139 (10), 138 (73), 123 (30), 97 (8), 74 (8), 73 (100); exact mass, 226.1574 (calcd for $C_{12}H_{26}Si_2$: 226.1573).

b. TMCS (2 equiv) followed by DeS. To a solution of MeC_3Li_3, prepared from 30 mmol of 1-butyne, was added 6.5 g (60 mmol) of TMCS at 0 °C and 2 h later, 9.2 g (60 mmol) of DeS. The mixture was stirred for 16 h, extracted with hexane, dried ($MgSO_4$), and distilled to give 2.4 g of product, bp 25–40 °C (100 μm) (dry ice trapped). The excess DeS was removed by refluxing with 20 ml of 20% alcohol KOH. Extraction and redistillation gave 1.8 g of product, which was shown by GLC to contain a mixture of **7**, **8**,[1] and **9**[1] (ratio of products 1:1:3).

Acknowledgment. This work was supported by the U.S. Air Force Office of Scientiic Research (NC), Office of Aerospace Research, USAF, Grant No. AF-AFOSR 70-1904 and AF-AFOSR 74-2644.

References and Notes

(1) Preceding paper in this issue.

(2) R. West and P. C. Jones, *J. Am. Chem. Soc.*, **91**, 6156 (1969).

(3) K. K. Anderson and S. W. Fenton, *J. Org. Chem.*, **29**, 3270 (1964).

(4) E. J. Corey and H. A. Kirst, *Tetrahedron Lett.*, 5041 (1968).

(5) H. M. Schmidt and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **86**, 1138 (1967).

(6) R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, **69**, 1827 (1967).

(7) Tse-Lok Ho, *Chem. Rev.*, **75**, 1 (1975).

(8) J. Klein and S. Brenner, *Tetrahedron*, **26**, 2345 (1970); *J. Org. Chem.*, **36**, 1319 (1971).

(9) L. Brandsma and E. Mugge, *Recl. Trav. Chim. Pays-Bas*, **92**, 628 (1973).

(10) A. J. Quillinan, E. A. Khan, and F. Scheinmann, *Chem. Commun.*, 1030 (1974); S. Bhanu and F. Scheinmann, *ibid.*, 817 (1975).

(11) Unfortunately, similar experiments utilizing C_3Li_4 and MeC_3Li_3 could not be performed since these polyanions do not give simple derivatization products on reaction with alkyl halides.[1]

(12) J. H. van Boom, P. P. Montijn, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **84**, 31 (1965).

(13) L. H. Sommer, P. A. DiGiorgio, W. A. Strong, R. E. van Strein, D. L. Bailey, H. K. Hall, E. W. Pictrusza, and G. T. Kerr, *J. Am. Chem. Soc.*, **68**, 475 (1946).