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Polylithium Compounds. 8. Synthesis of Allenes and Acetylenes from Perlithiopropyne, Trilithiobutyne, and Dilithio-3-methylbutyne[1,2]

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Abstract: The polylithiation of 1- and 2-butyne to give trilithiobutyne, MeC_3Li_3, and 3-methylbutyne to give dilithio-3-methylbutyne, $Me_2C_3Li_2$, have been investigated. Reactions of these polymetalated hydrocarbons and the lithiocarbon C_3Li_4 with dialkyl sulfates, chlorosilanes, and chlorogermanes yield polysubstituted allenes and acetylenes, in ratios dependent on the steric size of the derivatizing agents. Reaction of C_3Li_4 and $Me_2C_3Li_2$ with ethyl iodide produced oxidative coupling products. The infrared spectra of polylithiated acetylenes are reinterpreted in terms of propargylide and allenic anions.

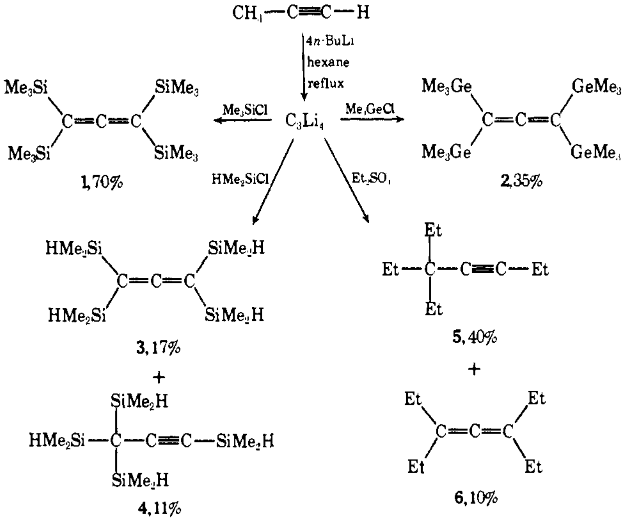
Introduction

The chemistry of poly- and perlithiated hydrocarbons has been a subject of continuing interest in recent years. Since West, Carney, and Mineo[3,4] prepared C_3Li_4, by the dropwise addition of propyne to four equivalents of *n*-butyllithium and Eberly and Adams[5] polymetalated 1-butyne and 1,2-butadiene using *n*-butyllithium, numerous papers have appeared on the subject of polylithiation.[6-14] Especially exciting is a recent paper by Shimp and Lagow who reported C_3Li_4 to be the major product in the high-temperature reaction of lithium atoms with carbon vapor.[15] In this paper we report the preparation of dilithio-3-methylbutyne, $Me_2C_3Li_2$, from 3-methylbutyne; trilithiobutyne, MeC_3Li_3, from both 1- and 2-butyne; and the use of C_3Li_4, MeC_3Li_3, and $Me_2C_3Li_2$ as intermediates in the synthesis of allenes and acetylenes. In addition we have reexamined the infrared spectra of these and other polylithium compounds and propose structures for these species.

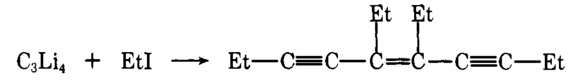
Results

Tetralithiopropyne (C_3Li_4). The lithiocarbon C_3Li_4 reacts with organic or organometallic substrates in the presence of tetrahydrofuran (THF) to give either allenic or acetylenic derivatives or both. With trimethylchlorosilane[4] and trimethylchlorogermane the products are tetrasubstituted allenes **1** and **2** (see Scheme I). With dimethylchlorosilane both the allenic **3** and acetylenic **4** tetrakis derivatives are observed. Reaction of C_3Li_4 with diethyl sulfate yielded the first hydrocarbon derivatives, the acetylene **5** and the allene **6**.[16] ^1H NMR, IR, UV, and mass spectral data for all compounds shown are in full agreement with proposed structures. Yields have not been optimized.

Scheme I



Addition of C_3Li_4 to an excess of ethyl iodide in THF at −78 °C resulted in no simple derivatives; however, a compound of formula $C_{14}H_{20}$ was isolated in 13% yield. The ^1H NMR spectrum of this coupling product consists of two equally intense overlapping quartets at δ 1.0 and 1.2 (12 H), and two overlapping quartets at δ 2.0–2.6 (8 H). The IR shows an internal acetylene stretch at 2200 cm^{-1}. The UV spectrum has a λ_{max} at 263 nm with a shoulder at 273 nm (ε 11 400 and 9650, respectively), suggesting a triene skeleton.[19] From these data the product was identified as 5,6-diethyl-5-decen-3,7-



$$C_3Li_4 + EtI \longrightarrow Et{-}C{\equiv}C{-}\overset{Et}{C}{=}\overset{Et}{C}{-}C{\equiv}C{-}Et$$

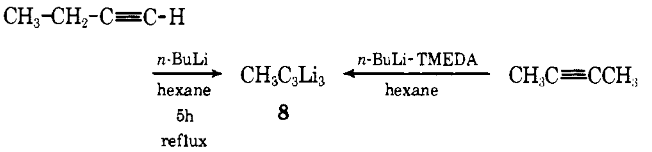
7,13%

diyne (7), the stereochemistry about the carbon-carbon double bond being undetermined.

Many other reactions of C_3Li_4 were attempted. Addition of C_3Li_4 to benzaldehyde at −78 °C gave a black solution from which benzyl alcohol, benzyl benzoate, and benzoin were isolated, but no addition products were obtained. The isolation of reduction and condensation products indicates that electron-transfer processes occur readily. Simple derivatization products were not obtained from reactions of C_3Li_4 with ethyl tosylate, triethyl phosphate, benzyl chloride, ethyl bromide, ethyl chloride, *n*-propyl bromide, *n*-propyl chloride, and carbon dioxide. These reactions were not pursued further.

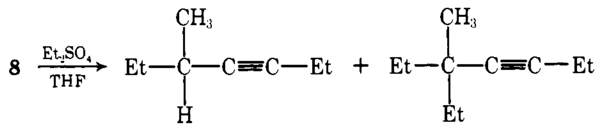
Trilithiobutyne (MeC_3Li_3) from 1-Butyne. We have succeeded in polylithiating 1-butyne with both *n*-butyllithium and *tert*-butyllithium. Eberly and Adams[5] reported that *n*-butyllithium forms a 1:1 adduct with dilithiobutyne after 210 h at room temperature rather than undergoing trimetalation. Jones and West[4] observed that trilithiated butyne (8) could be obtained from 1-butyne and *tert*-butyllithium. We found that reaction of 1-butyne witlh 3 equiv of *n*-butyllithium followed by 5 h reflux results in the evolution of 2.7 equiv of butane. An infrared spectrum of the resulting red-orange solution (vide infra) showed the major species present to be **8**. Lithiation utilizing *tert*-butyllithium results in a yellow precipitate which turns orange upon reflux. The infrared spectrum of this precipitate shows absorptions which indicate that both the di- and trilithiated species are present.

Trilithiobutyne from 2-Butyne. Under the conditions used for polylithiation of propyne or 1-butyne, 2-butyne is recovered unchanged,[4,5] but when the strongly coordinating solvent TMEDA (*N,N,N',N'*-tetramethylethylenediamine)[20] is added, polylithiation occurs. Thus, treatment of 2-butyne with *n*-butyllithium-TMEDA (Li:N 2:1) complex results in a thick reddish-brown oil. Because TMEDA is slowly metalated by organolithium compounds,[21,22] evolution of *n*-butane cannot be used here as a reliable guide to the extent of lithiation. However, a combination of infrared study and derivatization reactions, vide infra, strongly indicate that **8** is the major product.



$$CH_3{-}CH_2{-}C{\equiv}C{-}H \xrightarrow[\text{hexane, 5h, reflux}]{n\text{-BuLi}} \underset{\mathbf{8}}{CH_3C_3Li_3} \xleftarrow[\text{hexane}]{n\text{-BuLi-TMEDA}} CH_3C{\equiv}CCH_3$$

Independent of the method of generation, derivatization of polylithiated butyne with diethyl sulfate in THF resulted in diethyl and triethyl products **9** and **10**. Comparing the yields and product ratios from the three methods of preparation of MeC_3Li_3 (Table I), it is clear that starting from 1-butyne, *n*-BuLi is a better metalating agent than *t*-BuLi. The decreased yield of **10** from the 1-butyne-*tert*-butyllithium preparation results from incomplete formation of MeC_3Li_3. This incomplete lithiation is most likely due to the insolubility of the partially metalated intermediates in *tert*-butyllithium. Yields of **9** and **10** from trilithiated 2-butyne are similar to those obtained from *n*-butyllithium and 1-butyne.



$$\mathbf{8} \xrightarrow[THF]{Et_2SO_4} Et{-}\overset{CH_3}{\underset{H}{C}}{-}C{\equiv}C{-}Et + Et{-}\overset{CH_3}{\underset{Et}{C}}{-}C{\equiv}C{-}Et$$

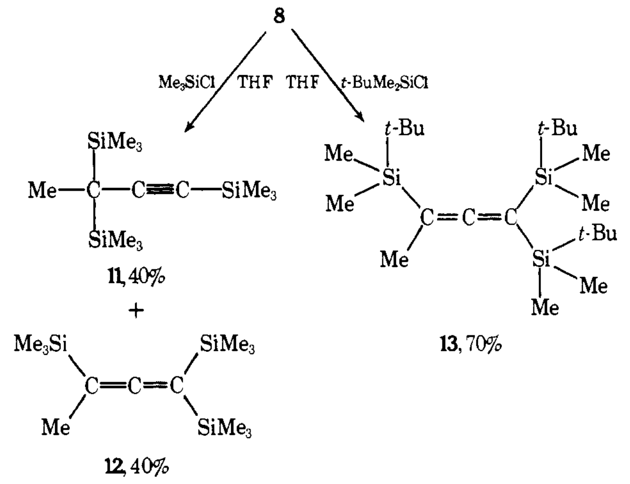
9 10

Table I. Diethyl Sulfate Derivatization of MeC_3Li_3

Method of prep of MeC_3Li_3	Yield 9	Yield 10
1-Butyne–*n*-BuLi	13	46
1-Butyne–*t*-BuLi	42	22
2-Butyne–*n*-BuLi/TMEDA	16	45

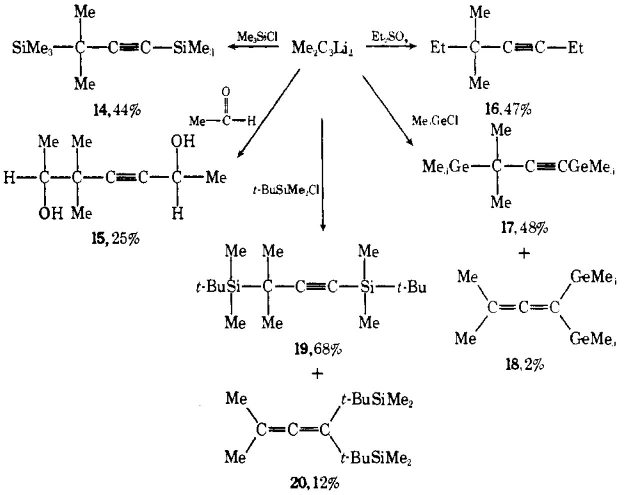
Derivatization of **8** with trimethylchlorosilane gave equal amounts of two trisilylated products, **11** and **12** (see Scheme II), while with *tert*-butyldimethylchlorosilane, only the less strained allenic compound **13** was observed. The two methyl groups on each geminal silicon in **13** are diastereotopic,[23] and in benzene or toluene a cluster of three overlapping singlets is observed.

Scheme II



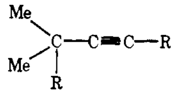
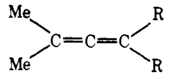
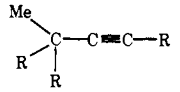
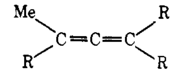
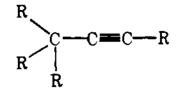
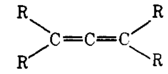
Dilithio-3-methylbutyne. Dilithio-3-methylbutyne ($Me_2C_3Li_2$), a red solution or orange solid, was prepared by the dropwise addition of 3-methyl-butyne to 2 equiv *n*-butyllithium; in a typical experiment 1.7 equiv of butane was evolved upon reflux. Reaction of $Me_2C_3Li_2$ with trimethylchlorosilane, acetaldehyde, diethyl sulfate, trimethylchlorogermane, and *tert*-butyldimethylchlorosilane resulted in the acetylenic products **14**, **15**, **16**, **17**, and **19** (Scheme III). With trimethylchlorogermane and *tert*-butyldimethylchlorosilane the product also contained small amounts of the allenic derivatives **18** and **20** as determined by ^1H NMR and IR spectroscopy.

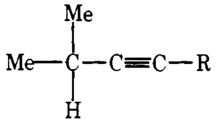
Scheme III



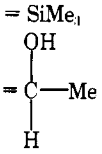
Smaller amounts of monoderivatized products **21**, **22**, **23**, and **24** were also isolated from monolithiated 3-methylbutyne.

Table II. Relative Percentages of Derivatization Products from $\mathrm{Me_2C_3Li_2}$, $\mathrm{MeC_3Li_3}$, and $\mathrm{C_3Li_4}$

Derivatizing agent	R	Acetylene	Allene
$\mathrm{Me_2C_3Li_2}$ →		 +	
$\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{MeC}}}\mathrm{\text{-}H}$	$\mathrm{HO\overset{\overset{Me}{\vert}}{C}H}$	100	0
$\mathrm{Et_2SO_4}$	Et	100	0
$\mathrm{Me_3GeCl}$	$\mathrm{Me_3Ge}$	96	4
$\mathrm{Me_3SiCl}$	$\mathrm{Me_3Si}$	100	0
t-$\mathrm{BuMe_2SiCl}$	t-$\mathrm{BuMe_2Si}$	85	15
$\mathrm{MeC_3Li_3}$ →		 +	
$\mathrm{Et_2SO_4}$	Et	100	0
$\mathrm{Me_3SiCl}$	$\mathrm{Me_3Si}$	50	50
t-$\mathrm{BuMe_2SiCl}$	t-$\mathrm{BuMe_2Si}$	0	100
$\mathrm{C_3Li_4}$ →		 +	
$\mathrm{Et_2SO_4}$	Et	80–100	20–0
$\mathrm{HMe_2SiCl}$	$\mathrm{HMe_2Si}$	40	60
$\mathrm{Me_3GeCl}$	$\mathrm{Me_3Ge}$	0	100
$\mathrm{Me_3SiCl}$	$\mathrm{Me_3Si}$	0	100



21, R = $\mathrm{SiMe_3}$

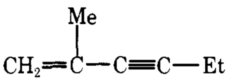


22, R = $\mathrm{\overset{\overset{OH}{\vert}}{\underset{\underset{H}{\vert}}{C}}\text{—}Me}$

23, R = Et

24, R = $\mathrm{GeMe_3}$

Reaction of $\mathrm{Me_2C_3Li_2}$ with ethyl iodide gave **23** and **16**, as well as two unexpected products, **25** and **26**. Compound **25** was readily identified as the vinyl acetylene from its IR, ^{1}H NMR, and UV spectra. The mass spectrum of **26** showed a molecular ion at m/e 190, indicating a molecular formula of $\mathrm{C_{14}H_{22}}$. The ^{1}H NMR consisted of a quartet at δ 2.1 (4 H), a singlet at δ 1.2 (12 H), and a triplet at δ 1.1 (6 H). The infrared spectrum had no absorptions in the allene, acetylene, or vinyl regions; the UV had a weak absorption at $\lambda_{\max}$ 226 (ϵ 330). These data strongly suggest that the product **26** is the oxidative coupling product, 5,5,6,6-tetramethyldeca-3,7-diyne.



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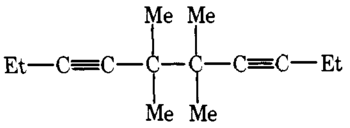

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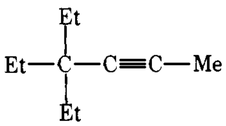

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Discussion and Conclusions

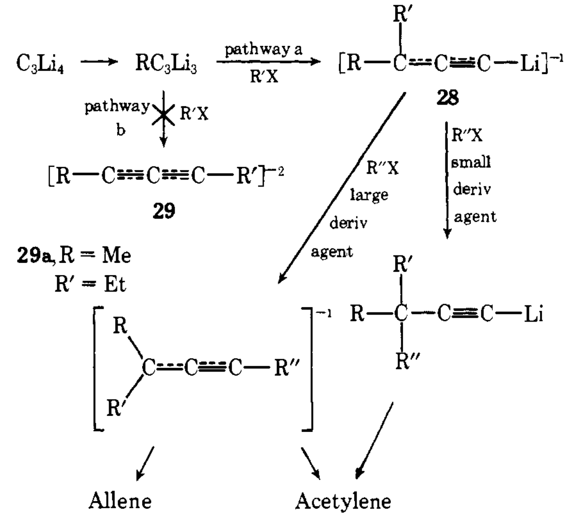
Allene to Acetylene Ratios. Table II shows the allene to acetylene product ratios for derivatizations of $\mathrm{Me_2C_3Li_2}$, $\mathrm{MeC_3Li_3}$, and $\mathrm{C_3Li_4}$. Clearly, in all cases, as the size of the derivatizing agent increases, the amount of allenic product increases. For $\mathrm{Me_2C_3Li_2}$, acetylenes are observed except with t-$\mathrm{BuMe_2SiCl}$. Apparently, the two methyl groups at carbon atom 3 of $\mathrm{Me_2C_3Li_2}$ are small enough that preferential derivatization takes place here unless a very bulky derivatizing agent is used. With $\mathrm{MeC_3Li_3}$ and a small R group, such as ethyl, only acetylenic products are formed while with a large R group, e.g., t-$\mathrm{BuMe_2Si}$, exclusive formation of the allenic isomer is observed. Trimethylsilyl, which is of intermediate size, gives a mixture. $\mathrm{C_3Li_4}$ again gives predominantly acetylenic products with small derivatizing agents and allenic products with larger ones.

These results can best be explained by considering the course of derivatization for these polyanions. $\mathrm{C_3Li_4}$ must initially react to give $\mathrm{RC_3Li_3}$. Derivatization of $\mathrm{MeC_3Li_3}$ with diethyl sulfate results in only one tris product, **10**. Although two pathways for derivatization are possible (Scheme IV), no products having the methyl group at the acetylenic end (i.e., **27**) and no allenic products are formed.

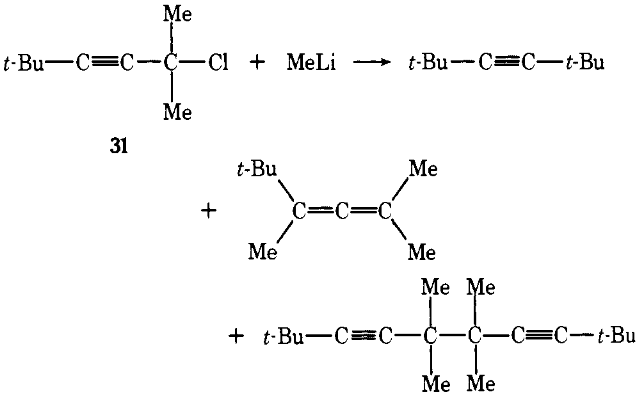
If pathway b were followed, the almost symmetric intermediate **29a** would result after monoderivatization. Further reaction with diethyl sulfate should give both **10** and **27**. However, **27** is not obtained, and pathway b can be eliminated. Pathway a was expected, a priori, to be preferred since the propargylide dianion **28** is formed rather then allenic dianion **29** (vide infra). Derivatization of **28** occurs at carbon atom 3 with small R″ resulting in the most stable monoanion, the 1-lithioacetylide. Further reaction must lead to the acetylene product. However, if steric hindrance in **28** prevents reaction at carbon atom 3, derivatization occurs at carbon atom 1 giving a propargyl anion, which undergoes further derivatization at the same position to give the allene product.

Oxidative Coupling with Ethyl Iodide. Reaction of $\mathrm{Me_2C_3Li_2}$ with ethyl iodide produced two unexpected products, **25** and **26**. Both can readily be explained by assuming metal-halogen

Scheme IV



exchange[24] with formation of intermediate **30**. Under the strongly basic reaction conditions, **30** can either eliminate LiI to give **25** or couple with $Me_2C_3Li_2$ to eventually give **26**. A similar product was observed by Macomber[25] who reacted the propargyl chloride **31** with MeLi and obtained **32**. Reaction of **8** with ethyl iodide produced no simple derivatives. Several high molecular weight products were formed but none were major.



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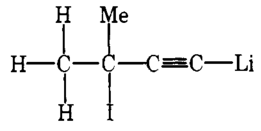
32

Formation of **7** from C_3Li_4 and ethyl iodide can also be explained by postulating lithium-halogen exchange. The resulting carbenoid, **33**, can couple with C_3Li_4 to give "C_6Li_6", **34**, and LiI. Another metal-halogen exchange and intramolecular elimination of LiI results in formation of "C_6Li_4", which finally derivatizes with ethyl iodide to give **7**. The structure of these intermediates or the extent of ethylation during these exchanges and eliminations is not known.



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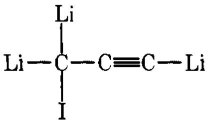

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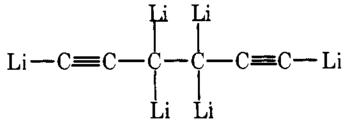

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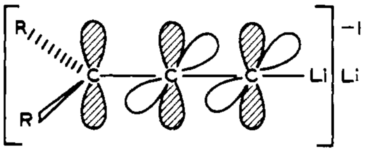
Infrared Spectra and Structure. The infrared spectra in the region 2200-1600 cm^{-1} for some lithiated acetylenes are summarized in Table III. These compounds fall into two categories: those that can directly form lithioacetylides (the terminal acetylenes) and those that must undergo hydrogen or alkyl shifts to form acetylides (the internal acetylenes). Because monolithiated internal acetylenes show infrared absorptions at the same frequency as monolithioallene, 1890 cm^{-1},[7] we believe lithiation of these compounds results in allenic anions. Further lithiation of these compounds lowers the infrared absorption band to about 1795 cm^{-1}. A bathochromic shift of about 80-90 cm^{-1}, the "lithium effect", takes place upon substitution of hydrogen by lithium [e.g., propyne (2130 cm^{-1}) → monolithioacetylide (2050) and allene (1970) → monolithioallene (1890)].[4] Therefore it appears that the dianions of internal acetylenes also have allenic structures.

Table III. Absorption Bands in the 1600–2200 cm^{-1} Region for Lithiated Internal and Terminal Acetylenes in Hexane

Compound	Acetylides and propargylides, cm^{-1}	Allenic anions, cm^{-1}
Monolithiated		
$H_3C—C≡C—Li$[a]	2050	
$Me_2CH—C≡C—Li$	2050	
$MeCH_2—C≡C—Li$	2040	
$PhCH_2—C≡C—Li$[b]	2050	
$[Me_3SiCH—C≡C—SiMe_3]Li$[a]		1870
$[(Me_3Si)_2C—C≡C—SiMe_3]Li$[a]		1850
$[Ph(Me_3Si)—C—C≡C—SiMe_3]Li$[b]		1850[c]
$[Ph—CH—C≡C—Ph]Li$[d]		1870
$[Me—CH—C≡C—Ph]Li$[d]		1870
Dilithiated		
$H_2C_3Li_2$[a]	1870	
$MeHC_3Li_2$	1850	
$Me_2C_3Li_2$	1850	
$PhHC_3Li_2$[b]	1900	
$[PhC—C≡C—Ph]Li_2$[d]		1790
$[Me—C—C≡C—Ph]Li_2$[d]		1795
$[Ph—C—C≡C—SiMe_3]Li_2$[b]		1790
$[Me_3Si—C—C≡C—SiMe_3]Li_2$[a]		1790
Trilithiated		
HC_3Li_3[a]	1750	
PhC_3Li_3[b]	1780	
$Me_3SiC_3Li_3$[a]	1770	
MeC_3Li_3	1770	
Tetralithiated		
C_3Li_4	1675	

[a] Reference 4. [b] Reference 11. [c] A band at 2000 cm^{-1} was also observed. This may be due to the propargyl anion, since the phenyl and silyl groups on carbon atom 3 might be expected to stabilize this anion relative to the allenyl anion. [d] Reference 31.

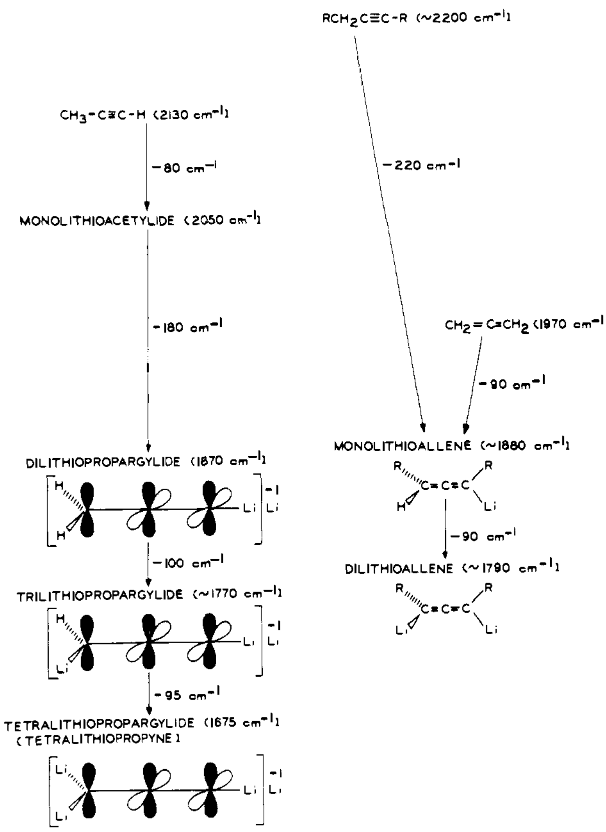
Lithiation of terminal acetylenes results in anions having a different structure. Initially monolithioacetylides, $R-C≡C^-Li^+$ are formed. Further lithiation gives a dianion having an absorption band lowered by *180* cm^{-1} (see Scheme V). This large bathochromic shift suggests that bond reorganization takes place upon dilithiation. We propose structure **34** for these dianions. Since this representation contains both acetylenic and propargylic lithium, we propose to call these compounds propargylides.



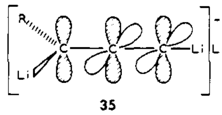
34

Some confusion has resulted from the fact that the infrared absorption of the propargylide *di*anion occurs at the same frequency as that of the allenic *mono*anion. However, since the extent of lithiation is different, these two anions must have different structures. Dilithiopropargylides which have another hydrogen at carbon atom 3 can undergo further lithiation in

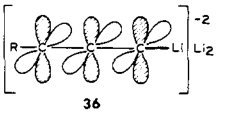
SCHEME 5
SUCCESSIVE LITHIATION OF PROPYNE VS ALLENE AND INTERNAL ACETYLENES



either an sp^2-type orbital to give trilithiopropargylide **35**, or in a p-type orbital to give a trilithiosesquiacetylene, **36**.[26] These

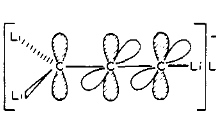


35

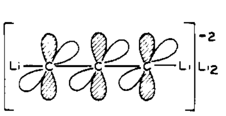


36

*tri*lithiated species coincidentally have infrared absorptions at the same frequency as *di*lithiated compounds having allenic structures. Further metalation can occur only in the case of propyne resulting in a tetralithio derivative which can be described either as a tetralithiopropargylide, **37**, or a tetralithiosesquiacetylene, **38**.



37



38

Intuitively, it is expected that dilithiated propargylides should be more stable than dilithiated allenes (and similarly for the trilithiated species). In the propargylide structure a pair of electrons is located in the highly electronegative carbon sp orbital and the other electron pair in a nonbonding, resonance stabilized propargyl orbital; in the allenic structure both electron pairs are located in carbon sp^2 orbitals. Since the acidity of an allylic hydrogen is approximately the same as the acidity of a vinylic hydrogen, i.e., p$K_a \simeq 36$, we expect a propargyl anion and an allenic anion to be of comparable stability. However the acetylide anion is much more stable than an sp^2 anion. Therefore, comparing the propargylide dianion and the allenic dianion, we expect formation of propargylides whenever possible. In agreement with this prediction, phenylallene *gem*-dilithiates to give the propargylide dianion rather than metalating at the benzylic position to give an allenic dianion.[27]

With perhaps one exception, monolithiated propargyl anions have not been observed, rather the allenic isomer seems to be preferred in hexane. However, West and Gornowicz[11] reported that monolithio-1,3-bis(trimethylsilyl)-3-phenylpropyne showed infrared absorptions at both 2000 and 1850 cm^{-1}. The lower frequency absorption can be assigned to the monolithiated allene while the former may result from the elusive propargyl anion, where phenyl and silicon both stabilize the charge at carbon atom 3.

The product distribution from the two types of anions is also very different. Propargylide anions derivatize to give acetylenic products exclusively unless steric interactions favor allenic products (see previous section), while allenic anions with unhindered derivatizing agents give both allenic and acetylenic products.[11,28,29]

Considering now the new polylithiated hydrocarbons reported in this paper, we believe MeC_3Li_3 is a trilithiated propargylide (IR, 1750 cm^{-1}) and $MeHC_3Li_2$ (the dilithiated intermediate from 1-butyne) and $Me_2C_3Li_2$ are dilithiated propargylides (IR, 1850 cm^{-1}) in hexane.[4,30]

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 and $LiAlH_4$, respectively, before use. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Gas chromatographic analysis and separations were made on a Varian Aerograph Model A-700 chromatograph with thermal conductivity detectors, or 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 A; (d) 15 ft × ⅜ in. 20% SE 30 on Chromosorb W; (e) 25 ft × ½ in. 20% QF-1 on Chromosorb W; (f) 25 ft × ⅜ in. 20% SE 30 on Chromosorb W, and (g) 25 ft × ⅜ in. Apiezon L on Chromosorb W.

Tetralithiopropyne was prepared by the method of West and Jones.[4]

The gases propyne and 1-butyne, Matheson Gas Products, were measured by condensing them into a graduated trap at −78 °C where the density of the liquid was known. The desired volume of liquid was warmed slowly to room temperature, and the gas was passed from the trap through Tygon tubing to a gas dispersion tube which was immersed in dry hexane contained in a dropping funnel attached to the reaction vessel. By allowing the condensed liquid to warm slowly, it was possible to control the rate of addition of the gas to the hexane solution. Any gas which was not dissolved in the solvent passed through the pressure-equalizing sidearm of the addition funnel into the butyllithium solution. A condenser containing a solid carbon dioxide-acetone mixture prevented loss of reactant during addition.

n-Butyllithium in hexane and *tert*-butyllithium in pentane were obtained from Foote Mineral Co. *N,N,N′,N′*-Tetramethylethylenediamine was purchased from Aldrich Chemical Co. and was distilled from barium oxide. 2-Butyne and isopropylacetylene were obtained from Farchan Research Laboratories. Trimethylchlorosilane, Dow Corning Corp., was distilled before use. *tert*-Butyldimethylchlorosilane was prepared by treating dimethyldichlorosilane with an equivalent amount of *tert*-butyllithium, purchased from Willow Brook Labs, Inc. Diethyl sulfate, Aldrich Gold Label, was stirred over anhydrous sodium carbonate until neutral to Congo red paper and then distilled. Ethyl iodide, Columbia Organic Chem. Co., was distilled before use. Trimethylchlorogermane, Alfa Ventron, was used as obtained.

Spectra were recorded by means of the following instruments: infrared, Perkin-Elmer 457, Beckman ir 33; ^{1}H NMR, Varian A-60, A-60A, T-60, or JEOL MH-100; mass spectra, AEI-MS 902 at 70 eV; ultraviolet-visible, Cary 14 or 15.

Infrared Spectra of Lithiated Acetylenes. The polylithiated acetylenes were prepared by the general procedures described below. Dilithioisopropylacetylene and trilithiated 1-butyne, both slurried in hexane, were syringed into a 0.5-mm NaCl infrared solution cell. Lithiated 2-butyne complexed with TMEDA was concentrated by removing the bulk of the solvent under reduced pressure. The viscous brown oil was then spread between two sodium chloride plates under a stream of nitrogen. The periphery of the plates was coated with a thin layer of Apiezon N grease. The following infrared absorptions were observed: lithiated propyne, 1675 (s);[4] lithiated isopropylacetylene, 2050 (w), 1850 cm^{-1}; lithiated 1-butyne (*n*-butyllithium as lithiating agent) 2030 (w), 1855 (m), 1740 (vs), 1630 (m) cm^{-1}; lithiated 1-butyne (*tert*-butyllithium as lithiating agent) 2030 (w), 1900 (vw), 1845 (m), 1740 (m), 1630 (m) cm^{-1}; lithiated 2-butyne (neat) 1970 (w), 1810 (sh), 1750 (s), 1630 (m) cm^{-1}. Addition of HMPA or THF to an aliquot of these solutions changed the infrared absorptions to 1955 and 1675 cm^{-1} for C_3Li_4, 1950 cm^{-1} for MeC_3Li_3, and 1910 and 2050 cm^{-1} for $Me_2C_3Li_2$.

Derivatization of C_3Li_4 with Trimethylchlorogermane. A solution of C_3Li_4 prepared from 10 mmol of propyne was added dropwise to 7.65 g (50 mmol) of trimethylchlorogermane in 50 ml of THF at −78 °C. After 24 h at room temperature, 100 ml of water was added, and the organic phase extracted with ether. The extracts were dried ($MgSO_4$) and distilled, bp 70–80 °C (90 μm), 2.1 g. Final purification was accomplished by preparative GLC on column d (250 °C). It was estimated that about 1.9 g (90% of area, 35% yield) of tetrakis(trimethylgermyl)allene, (3,5-bis(trimethylgermyl)-2,5-digerma-3,4-heptadiene, **2**) was present. The characteristic spectral data for **2** are: ^1H NMR (CCl_4) δ 0.23 (s); IR (CCl_4) 2975, 2895, 1880, 1400, 1235, 840–710 (broad) cm^{-1}; mass spectrum *m/e* (rel intensity) 512 (3), 512 (7), 511 (5), 510 (11), 509 (9), 508 (14), 507 (8), 506 (14), 505 (7), 504 (11), 503 (5), 502 (7), 501 (3), 500 (5), 499 (6), 698 (6), 497 (15), 496 (12), 495 (25), 494 (16), 493 (32), 492 (17), 491 (35), 490 (14), 489 (26), 488 (9), 487 (16), 486 (3), 485 (8), 121 (24), 119 (100), 118 (23), 117 (73), 115 (38), 57 (26), 44 (66), 43 (25), 41 (36), 40 (92). Anal. Calcd for $C_{15}H_{36}Ge_4$: C, 35.6; H, 7.12. Found: C, 35.4; H, 7.21.

Derivatization of C_3Li_4 with Dimethylchlorosilane. A solution of C_3Li_4 (0.04 mol) in hexane was added dropwise to a solution of dimethylchlorosilane (45 g, 0.48 mol) in THF at −78 °C. The dark red color of the organolithium reagent disappeared upon addition and a white precipitate was formed. After warming to room temperature, the solution was filtered and distilled, resulting in 4.2 g of product (28%), bp 80–130 °C (8 mm). This distillate was separated by preparative GLC (155 °C) on column f into two components, **3** (61% of total area) and **4** (39%), retention times 15.3 and 18.0 min, respectively.

Tetrakis(dimethylsilyl)allene(2,6-Dimethyl-3,5-bis(dimethylsilyl)-2,6-disila-3,4-heptadiene, 3).[32] ^1H NMR (CCl_4) δ 0.25 (d, *J* = 3.5 Hz, 24 H), 4.20 (m, 4 H); IR (CCl_4) 2170, 1885, 1245 cm^{-1}. Anal. Calcd for $C_{11}H_{28}Si_4$: C, 48.4; H, 10.3. Found: C, 48.3; H, 10.4.

2,6-Dimethyl-5,5-bis(dimethylsilyl)-2,6-disila-3-heptyne (4). ^1H NMR (CCl_4) δ 0.07 and 0.11 (d, *J* = 3.75 H, d, *J* = 3.6 Hz, 24 H), 4.15 (m, 4 H); IR (CCl_4) 2130, 2100, 1250 cm^{-1}. Anal. Calcd for $C_{11}H_{28}Si_4$: C, 48.4; H, 10.3. Found: C, 48.4; H, 10.3.

Derivatization of C_3Li_4 with Diethyl Sulfate. To 30 g (0.20 mol) of diethyl sulfate in 100 ml of THF at −78 °C was added a solution of C_3Li_4 prepared from 40 mmol propyne. After addition, the solution was warmed to room temperature and stirred overnight. The resulting yellow solution with gelatinous white precipitate was refluxed for 2 h. Two hundred ml of 10% KOH in 50% EtOH was added to hydrolyze excess diethyl sulfate and refluxing was continued for 2 h. The mixture was cooled, extracted with ether, and dried over $MgSO_4$. Distillation yielded 3.7 g of product, bp 20–35 °C (150 μm), which was separated by preparative GLC (170 °C) on column e into two components, **5** (64% of total area) and **6** (16%); combined yield 50%; retention times: 19.8 and 18.0 min, respectively. In other runs no allenic product was observed. The spectral data were the following.

5,5-Diethyl-3-heptyne (5). ^1H NMR (CCl_4) δ 2.2 (q, second order splitting present, 2 H), 1.6–1.0 (m, 9 H), 0.88 (t, 9 H); IR (CCl_4) 2990, 2920, 2870, 1460, 1445 sh, 1375, 1340, 1320, 910 cm^{-1}; mass spectrum *m/e* (rel intensity) 152 (15), 124 (10), 123 (100), 122 (13), 95 (13), 81 (74), 79 (10), 77 (90), 69 (9), 67 (18), 57 (8), 55 (20), 53 (9), 43 (13), 41 (19), 39 (7), 29 (9). Anal. Calcd for $C_{11}H_{20}$: C, 86.75; H, 13.25. Found: C, 86.69; H, 13.35.

Tetraethylallene (3,5-Diethyl-3,4-heptadiene, 6). ^1H NMR (CCl_4) 1.9 (q, *J* = 7 Hz, 8 H), 0.93 (t, *J* = 7 Hz, 12 H); IR (CCl_4) 2960, 2925, 2865, 1450, 1370, 1320, 1240, 930 cm^{-1}; mass spectrum *m/e* (rel intensity) 153 (6), 152 (55), 124 (10), 123 (100), 95 (21), 93 (9), 91 (11), 81 (74), 79 (16), 77 (16), 69 (15), 67 (25), 65 (7), 57 (8), 55 (30), 53 (14), 45 (19), 43 (15), 41 (34), 39 (14), 29 (15); exact mass, 152.1564 (calcd for $C_{11}H_{20}$: 152.1565).

Derivatization of C_3Li_4 with Ethyl Iodide. To a solution of 83 g (0.53 mol) of ethyl iodide in 100 ml of THF at −78 °C was added a hexane solution of C_3Li_4 prepared from 40 mmol of propyne. After stirring at room temperature for 16 h, the solution was amber brown in color with a precipitate of LiCl. Water (100 ml) was added, the organic phase was extracted with hexane and dried ($MgSO_4$). Removal of solvents gave 5.1 g of crude product. Distillation resulted in the isolation of *n*-butyl iodide, formed by metal–halogen exchange on unreacted *n*-butyllithium, and 0.5 g of product **7**, bp 75 °C (300 μm). The bulk of the product would not distill and decomposed upon further heating. Final purification of **7** was accomplished by preparative GLC on column f (190 °C).

5,6-Diethyl-5-decen-3,7-diyne (7). ^1H NMR (CCl_4) δ 1.1 and 1.2 (two overlapping 5, 12 H), 2.0–2.6 (two overlapping q, 8 H); IR (CCl_4) 2985, 2925, 2860, 2200, 1450, 1372, 1315, 1260, 1120, 840 cm^{-1}; the product has a carbon–carbon double bond, but due to its symmetrical nature no alkene stretch at 1600 cm^{-1} was observed: UV λ_{max} (EtOH) 263 nm (ε 11 400), 273 sh (9650); mass spectrum *m/e* (rel intensity) 189 (16), 188 (100), 173 (5), 159 (12), 144 (17), 131 (34), 130 (17), 129 (30), 128 (20), 91 (30), 77 (26); exact mass, 188.154 (calcd for $C_{14}H_{20}$: 188.156); $n^{23}D$ 1.4899.

Reaction of C_3Li_4 with Benzaldehyde. A solution of C_3Li_4 prepared from 80 mmol of propyne was added dropwise to a solution of benzaldehyde (68 g, 0.64 mol) in 200 ml of 1:1 THF–ether at −78 °C. The mixture turned black during addition and a Gilman color test I after completion of addition was negative.[33] After warming to room temperature, it was obvious that a black oily solid had formed. After 24 h of stirring, 100 ml of saturated NH_4CL and 100 ml of EtOAc were added. The organic layer was extracted three times with 200-ml portions of saturated NH_4Cl, three times with 200-ml portions of saturated $NaHSO_4$, and two times with 200 ml of H_2O. After drying ($MgSO_4$) the solvents were removed leaving a black oil. Distillation (1 Torr) gave three products. They were identified as benzyl alcohol (10.5 g, 0.10 mol), benzoin (1.5 g, 0.01 mol), and benzyl benzoate (7.5 g, 0.04 mol). No products derived from lithiated propyne could be isolated. These were presumably present in the black tarry residue.

General Procedure for Polylithiation of 2-Butyne. *n*-Butyllithium in hexane was placed in a reaction vessel equipped with an air-tight mechanical stirrer (Chesapeake) and a condenser containing solid carbon dioxide mixed with acetone. To this stirring solution, ¼ molar equiv of TMEDA (N:Li 1:2) was added dropwise with a syringe. The complex was allowed to stir for 30 min, resulting in the formation of pale-yellow solution with white suspension. A measured solution of 2-butyne in dry hexane was then added, with stirring, over a period of 20 to 30 min. After 4 h of stirring at room temperature, the solid carbon dioxide–acetone condenser was replaced by a water condenser. At the end of this time, the reaction mixture turned dark yellow with the formation of reddish brown viscous oil. The reaction mixture was then heated to reflux resulting in a dark brown solution with tarry dark brown oil.

General Procedure for Lithiation of 1-Butyne. a. Using *n*-butyllithium. To a 250-ml three-necked flask, equipped with a serum cap, dry ice condenser, dropping funnel, and magnetic stirrer, was added 112 ml of 1.6 M (0.18 mol) *n*-butyllithium. 1-Butyne (3.3 g, 4.8 ml, 0.06 mol) dissolved in 50 ml of cold hexane was added dropwise over 2 h. The solution was initially yellow; after 16 h reflux a gelatinous orange precipitate had formed. The trapped butane weighed 8.9 g (0.15 mol, 85% of 3 equiv).

b. Using *tert*-butyllithium. An identical procedure to that described above was used substituting 145 ml of 1.25 M (0.18 mol) *tert*-butyllithium for the *n*-butyllithium. A fine yellow precipitate formed immediately upon addition; after 5 h reflux this precipitate was bright orange.

Derivatization of MeC_3Li_3 with Diethyl Sulfate. a. From 2-butyne. Using the experimental procedures described above, 3.9 ml (0.05 mol) of 2-butyne in 50 ml of hexane and a complex of 150 ml of 1.6 M *n*-butyllithium (0.24 mol) and 8.9 ml (0.06 mol) of TMEDA were then heated at reflux for 12 h. The reaction mixture was cooled to room temperature and stirred overnight. With the temperature lowered to −78 °C, a solution of 66 ml (0.30 mol) of diethyl sulfate in 150 ml of THF was added, with stirring, over 30 min. The reaction mixture was allowed to slowly warm to room temperature then heated to gentle reflux for 1 h. A yellow solution with a white suspension, giving a negative Gilman color test,[33] was formed after cooling to room temperature. Sodium hydroxide (50 g) in a mixture of 200 ml of water and 20 ml of methanol was added. The solution was heated at reflux for 2 h to decompose excess diethyl sulfate. The organic layer was washed with dilute hydrochloric acid to remove excess amines, then washed with water and dried over anhydrous magnesium sulfate. Removing solvent gave 6.2 g of crude products. GC analysis (column d at 160 °C) showed that approximately 3.1 g (45%) of **10** and 0.9 g (16%) of **9** were present. Final separation of **9** and **10** was accomplished by preparative GLC. The following properties were obtained.

5-Methyl-3-heptyne (9). ^{1}H NMR (CCl$_4$) δ 2.5–1.85 (m, 3 H), 1.7–0.7 (m, 11 H); IR (CCl$_4$) 2990, 2935, 2880, 1443, 1380, 1335, cm^{-1}; mass spectrum *m/e* (rel intensity) 111 (5), 110 (M$^+$, 48), 95 (45), 81 (100), 79 (27), 67 (29), 55 (27), 53 (32), 41 (37); exact mass, 110.1098 (calcd for C_8H_{14}: 110.1095).

5-Ethyl-5-methyl-3-heptyne (10). ^{1}H NMR (CCl$_4$) δ 2.1 (m, 2 H), 1.8–0.8 (m, 13 H), 1.1 (s, 3 H); IR (CCl$_4$) 2995, 2940, 2860, 1460, 1375, 1320 cm^{-1}; mass spectrum *m/e* (rel intensity) 138 (M$^+$, 10) 110 (8.0), 109 (100), 108 (8.7), 95 (5), 94 (38), 92 (5.0), 81 (24), 79 (9), 77 (8), 69 (9), 67 (56), 65 (5), 55 (25), 53 (10), 43 (2), 41 (21); exact mass, 138.1410 (calcd for $C_{10}H_{18}$: 138.1408). Anal. Calcd for $C_{10}H_{18}$: C, 86.95; H, 13.04. Found: C, 86.65; H, 12.75.

b. From 1-butyne. The experimental procedure was similar to that used above. Analytical GLC of the distilled products on column a (180 °C) showed **9** and **10** were the major products. Using MeC_3Li_3 prepared from *n*-butyllithium the ratio of **10** to **9** was 2:1, using *tert*-butyllithium as the metalating agent the ratio was 1:2.

Derivatization of MeC_3Li_3 with Trimethylchlorosilane. A solution of 1.18 ml (15 mmol) of 2-butyne in 20 ml of hexane was allowed to react with a complex of *n*-BuLi (100 ml, 160 mmol) and TMEDA (5.8 ml, 4.0 mmol) according to the procedures described above. The reaction mixture was heated at reflux for 5 h. With the temperature lowered to −78 °C, the reaction mixture was slowly derivatized with 25.5 ml (0.20 mol) of trimethylchlorosilane in 90 ml of THF. A light brown solution with white suspension was present after warming to room temperature. The mixture was then heated at reflux for 2 h, and Gilman color test was negative at that time. To the reaction mixture was added dilute hydrochloric acid to remove excess amines. The mixture was then washed with water and dried over anhydrous magnesium sulfate. Crude distillation in vacuo yielded 5.4 g of impure products. Preliminary purification by preparative GLC (250 °C) on column f separated **11** and **12** as one component from other impurities. These two isomers were then separated and isolated by preparative GLC on column g at 200 °C. It was estimated by GLC that about 1.6 g (40%) each of **11** and **12** was present. The spectral data for 1,3,3-tris(trimethylsilyl)-1-butyne (**11**) were: ^{1}H NMR (CCl$_4$) δ 1.15 (s, 3 H), 0.09 (s, 9 H), 0.08 (s, 18 H); IR (neat) 2960, 2905, 2880, 2180, 2135, 1455, 1410, 1260, 1250, 1078, 925, 840, 790, 760, 690, 655 cm^{-1}; mass spectrum *m/e* (rel intensity) 270 (vw, M$^+$), 150 (9), 149 (15), 148 (100), 111 (11), 83 (8), 74 (5), 73 (73), 64 (18), 56 (14), 53 (5).

The spectral data of 1,1,3-tris(trimethylsilyl)-1,2-butadiene (**12**) were: ^{1}H NMR (CCl$_4$) δ 1.65 (s, 3 H), 0.14 (s, 18 H), 0.2 (s, 9 H); IR 2960, 2925, 2905, 2865, 1900, 1450, 1370, 1300, 1260, 1250, 1100, 960, 935, 900, 840, 760, 690, 667, 620 cm^{-1}; mass spectrum *m/e* (rel intensity) 270 (vw, M$^+$), 182 (14), 155 (8), 151 (17), 149 (2), 148 (6), 147 (9), 111 (8), 97 (4), 83 (8), 82 (4), 80 (5), 75 (5), 74 (6), 73 (19), 70 (11), 69 (100), 67 (6), 66 (8), 59 (10), 58 (4), 55 (20). Anal. Calcd for $C_{13}H_{30}Si_3$ (mixture of **11** and **12**): C, 57.69; H, 11.17; Si, 31.13. Found: C, 57.46; H, 10.82; Si, 31.48.

Derivatization of MeC_3Li_3 with *tert*-Butyldimethylchlorosilane. The same experimental technique was used as reported above. The reaction mixture consisted of 1.18 ml (15 mmol) of 2-butyne, dissolved in 20 ml of hexane, in 100 ml of 1.6 M *n*-butyllithium (160 mmol) complexed with 5.8 ml (40 mmol) of TMEDA. The mixture was heated at reflux for 32 h, then cooled to −78 °C and derivatized with 27 g (180 mmol) of *tert*-butyldimethylchlorosilane dissolved in 120 ml of THF. Workup as described previously yielded 7.5 g of crude material. GC analysis (column e, 230 °C) showed that approximately 4.2 g (71%) of **13** was present. Final purification was accomplished by preparative GLC. The spectral data for 1,1,3-tris(*tert*-butyldimethylsilyl)-1,2-butadiene were the following: ^{1}H NMR (d$_6$ benzene) δ 1.78 (s, 3 H), 1.08 (s, 18 H), 1.06 (s, 3, 9 H), 0.24–0.22 (three broad, overlapping singlets, 18 H); IR (CCl$_4$) 2970, 2940, 2900, 2870, 1880, 1478, 1467, 1406, 1397, 1367, 1320, 1213, 1137, 1090, 1072, 1010, 956, 940, 887, 680, 650, 590, 520 cm^{-1}; mass spectrum *m/e* (rel intensity) 396 (6, M$^+$), 341 (4), 340 (7), 339 (21), 225 (4), 210 (4), 209 (17), 186 (4), 185 (18), 155 (9), 127 (9), 115 (5), 99 (10), 97 (15), 75 (5), 74 (9), 73 (100), 59 (7), 41 (5); exact mass, 396.3063 (calcd for $C_{22}H_{48}Si_3$: 396.3064).

General Procedure for Lithiation of 3-Methyl-1-butyne. Into a 500-ml three-neck flask, equipped with a serum cap, dry ice-cooled condenser, pressure-equalized dropping funnel, and magnetic stirrer, was syringed 220 ml of 1.6 M *n*-butyllithium (0.35 mol). To 50 ml of cold hexane in the dropping funnel was added 10.9 g (15.3 ml, 0.16 mol) of isopropylacetylene previously cooled to −78 °C. The acetylene solution was added dropwise over 2 h. Upon completion of addition, the dry ice condenser was replaced by a water-cooled condenser attached to a cold trap at −78 °C. After 5 h reflux, the solution was bright red-orange and 15.7 g (0.27 mol, 85% of 2 equiv) of butane had been collected.

Derivatization of $Me_2C_3Li_2$ with Trimethylchlorosilane. A hexane solution of $Me_2C_3Li_2$ prepared from isopropylacetylene was added dropwise to a mixture of 50 ml of THF and 17.5 g (20.6 ml, 160 mmol) of trimethylchlorosilane at −78 °C. Initially, the orange color of the dilithiated compound disappeared rapidly; however, during the course of the reaction its disappearance became slower and a yellow color was observed in the solution. Upon completion of addition and warming to −20 °C, the solution decolorized. After filtration, the solution was distilled. The fraction (7.52 g), bp 25–65 °C (8 Torr), was collected and separated into two components by preparative GLC on column d (190 °C). Disilylated product **14** (3.7 g, 44%) and monosilylated product **21** (1.4 g, 26%) were isolated. The spectral data were the following.

2,2,5,5,6,6,-Hexamethyl-2,6-disila-3-heptyne (14). ^{1}H NMR (CCl$_4$) δ 0.05 (s, 9 H), 0.10 (s, 9 H), 1.13 (s, 6 H); IR (CCl$_4$) 2150, 1250, 850 cm^{-1}; mass spectrum *m/e* (rel intensity) 212 (24, M$^+$), 155 (20), 124 (100), 73 (91); exact mass, 212. 145 (calcd for $C_{11}H_{24}Si_2$: 212.142); n^{22}D 1.4375. Anal. Calcd for $C_{11}H_{24}Si_2$: C, 62.12; H, 11.38; Si, 26.45. Found: C, 61.97; H, 11.25; Si, 26.17.

2,2,5-Trimethyl-2-sila-3-hexyne (21).[34] ^{1}H NMR (CCl$_4$) δ 0.12 (s, 9 H), 1.16 (d, J = 6.8 Hz, 6 H), 2.51 (septet, J = 6.8 Hz, 1 H); IR (CCl$_4$) 2220, 1392, 1375, 1250 cm^{-1}; mass spectrum *m/e* (rel intensity) 141 (3), 140 (18, M$^+$), 126 (11), 125 (100), 109 (6), 97 (7), 95 (5), 83 (19), 73 (10); exact mass, 140.105 (calcd for $C_8H_{16}Si$: 140.102).

Derivatization of $Me_2C_3Li_2$ with Acetaldehyde. To a solution of $Me_2C_3Li_2$ prepared from 5.4 g (80 mmol) of 3-methylbutyne was added 50 ml of THF and then dropwise 10 ml (180 mmol) of acetaldehyde at −78 °C. After warming to room temperature and stirring for 16 h, dilute HCl was added to the mixture. Extraction, drying, and rotary evaporation resulted in 14.4 g of crude product. Kugelrohr distillation gave two fractions: 4 g, bp 25–30 °C (150 μm) and 3.2 g, bp 70–80 °C (100 μm). Analysis by GLC column d (160 °C) showed the lower boiling fraction contained 2.1 g of **22** (24% yield) and the higher boiling fraction contained 95% **15** (25% yield). The following data were obtained.

5,5-Dimethyl-3-heptyne-2,6-diol (15). ^{1}H NMR (CCl$_4$) δ 1.10 (s, 3 H), 1.18 (s, 3 H), 1.20 (d, J = 6.0 Hz, 3 H), 1.38 (d, J = 6.5 Hz, 3 H), 3.2–3.8 (broad, m, 2 H), 4.2–4.65 (broad q, 2 H); ^{1}H NMR (CCl$_4$ D$_2$O) 3.45 (q, J = 6.0 Hz, 1 H), 4.42 (q, J = 6.5 Hz, 1 H), all other peaks unchanged; IR 3640 (sharp), 3400 (broad), 2240 (w), 1450, 1370, 1325, 1075, 970, 920, 895, 855 cm^{-1}; mass spectrum *m/e* (rel intensity) 156 (very weak), 123 (3.6), 112 (4.2), 110 (4.2), 97 (8.4), 95 (15), 94 (100), 93 (15), 91 (69), 89 (15), 79 (31), 77 (17); exact mass, 156.1157 (calcd for $C_9H_{16}O_2$: 156.1150).

5-Methyl-3-hexyne-2-ol (22).[35] ^{1}H NMR (CCl$_4$) δ 1.15 (d, J = 6.8 Hz, 6 H), 1.4 (d, J = 6.5 Hz, 3 H), 2.55 (m, 1 H), 3.3 (broad s, 1 H), 4.1–4.7 (very broad s, 1 H); ^{1}H NMR (CCl$_4$ + D$_2$O) δ 3.3 (no peak), 4.4 (q, J = 6.5 Hz, 1 H), all other peaks unchanged; IR (CCl$_4$) 3360 (sharp), 3500 (broad), 2240, 1445, 1380, 1360, 1320, 1250, 1185, 1130, 1095, 1040, 970, 890 cm^{-1}; mass spectrum *m/e* (rel intensity) 112 (0.33), 111 (1.2), 110 (0.90), 97 (40), 95 (3.5), 79 (8.5), 75 (8.7), 69 (16), 67 (19), 55 (8.2), 53 (21), 51 (8.7), 45 (11), 43 (100), 41 (60), 39 (21); exact mass, 112.090 (calcd for $C_7H_{12}O$: 112.088).

Reaction of $Me_2C_3Li_2$ with Diethyl Sulfate. $Me_2C_3Li_2$ prepared from 80 mmol of 3-methylbutyne was added dropwise to a solution of 100 ml of THF and 62 g (400 mmol) of diethyl sulfate at −78 °C. The solution initially turned dark, but after warming to room temperature and stirring overnight, a light yellow solution with a white gelatinous precipitate was present. Ten ml of water was added followed by 350 ml of 10% alcoholic KOH. The solution was refluxed for 3 h to hydrolyze excess diethyl sulfate. The organic phase was separated, washed with water, and dried over $MgSO_4$. Spinning band distillation removed most of the solvents leaving 11.2 g of crude product. Distillation, 20–35 °C (8 Torr), resulted in 8.8 g of product which was separated by preparative GLC on column d (150 °C), affording 5,5-dimethyl-3-heptyne (**16**) (47%) and 2-methyl-3-hexyne (**23**) (32%). The following spectral data were observed.

5,5-Dimethyl-3-heptyne (16).[36] ^{1}H NMR (CCl_4) δ 1.1 (s, 6 H), 0.8–1.6 (m, 8 H), 2.12 (q, J = 7.7 Hz, 2 H); IR (CCl_4) 2220 (w), 1375,355 cm^{-1}; mass spectrum m/e (rel intensity) 125 (3), 124 (32, M$^+$), 109 (13), 95 (100), 67 (44), 55 (35), 41 (25); exact mass, 124.128 (calcd for C_9H_{16}: 124.125).

2-Methyl-3-hexyne (23).[37,38] ^{1}H NMR (CCl_4) δ 1.1 (t, J = 8 Hz, 3 H), 1.1 (d, J = 6.5 Hz, 6 H), 2.1 (q, J = 8 Hz, 2 H), 2.3 (m, J = 6.5 Hz, 1 H); IR (CCl_4) 2250 (vw), 1380, 1365 cm^{-1}; mass spectrum m/e (rel intensity) 96 (79), 95 (26), 81 (100), 79 (37), 67 (62), 55 (35), 53 (53), 41 (65), 39 (44).

$Me_2C_3Li_2$ and Trimethylchlorogermane. A solution of $Me_2C_3Li_2$ prepared from 26 mmol of isopropylacetylene was added dropwise to 53 mmol (8.2 g) of trimethylchlorogermane in 25 ml of THF at −78 °C. The organolithium solution decolorized immediately upon addition. After warming to room temperature and stirring for 18 h, the solution was filtered and the solvents were removed by spinning band distillation. The remaining solution was distilled into two fractions, bp 20–35 °C (2 mm) (6.9 g), bp 65 °C (300 μm) (3.7 g). The lower boiling fraction contained *n*-butyltrimethylgermane and **24**. Separation was effected by preparative GLC on column d (90 °C). Approximately 1.8 g (37% yield) of **24** was present. The higher boiling fraction was almost pure **17** (50% yield). Analytical samples of **17** were purified by preparative GLC on column d (190 °C). Only a single peak was observed on this column, but ^{1}H NMR and IR analyses indicated that there was a 3–4% impurity of the allene, 2,5,5,-trimethyl-4-trimethylgermyl-2,3-hexadiene (**18**). The following data were observed.

2,2,5,5,6,6-Hexamethyl-2,6-digerma-3-heptyne (17). ^{1}H NMR (CCl_4) δ 0.16 (s, 9 H), 0.28 (s, 9 H), 1.19 (s, 2 H), also small peaks at δ 0.21 (s), 1.65 (s) due to allene **18**; IR (CCl_4) 2980, 2960, 2915, 2865, 2805, 2170, 2140, 1460, 1450, 1405, 1360, 1335, 1230, 1200 cm^{-1}; also a small peak at 1930 cm^{-1} (allene stretch) was present; mass spectrum m/e (rel intensity) 306 (3.5), 305 (2), 304 (9), 303 (5), 302 (10), 301 (5), 300 (14), 299 (3), 298 (7), 296 (3), 291 (3), 290 (2), 289 (6), 288 (4), 287 (9), 286 (4), 285 (8), 284 (2), 283 (5), 281 (2), 172 (22), 171 (10), 170 (100), 169 (34), 168 (77), 167 (9), 166 (64), 120 (19), 119 (4), 118 (84), 117 (22), 116 (66), 114 (52), 112 (13). Anal. Calcd for $C_{11}H_{24}Ge_2$: C, 43.80; H, 8.03. Found: C, 44.00; H, 8.12.

2,5,5,-Trimethyl-2-germa-3-hexyne (24). ^{1}H NMR (CCl_4) δ 0.60 (s, 9 H), 1.47 (d, J = 6.7 Hz, 6 H), 2.82 (m, 1 H); IR 2975, 2925, 2910, 2890, 2805, 2160, 1460, 1440, 1410, 1380, 1360, 1310, 1235, 1165, 1100, 950 cm^{-1}; mass spectrum m/e (rel intensity) 186 (5), 185 (2), 184 (4), 182 (3), 173 (20), 172 (8), 171 (100), 170 (27), 169 (74), 167 (57), 129 (13), 128 (3), 127 (10), 125 (10), 119 (9), 118 (2), 117 (8), 115 (7), 113 (8), 112 (3), 111 (6), 105 (8), 104 (4), 103 (7), 101 (8), 99 (8), 97 (6), 89 (18), 88 (5), 87 (14), 85 (10), 67 (7), 57 (5); exact mass, 186.0471 (calcd for C_8H_6Ge: 186.0470).

Reaction of $Me_2C_3Li_2$ with Ethyl Iodide. To 150 g (0.96 mol) of ethyl iodide dissolved in 200 ml of THF at −78 °C was added a solution of $Me_2C_3Li_2$ prepared from 80 mmol of isopropylacetylene. A Gilman color test[35] taken 2 h after addition was still positive. However after 16 h at room temperature, a second color test was negative. The solution was washed with three 100-ml portions of water, passed through $CaCl_2$, and dried ($MgSO_4$). The solvents were removed by distillation at 760 Torr, and the low boiling products were collected in one fraction, 12.2 g, bp 25 °C 200 μm. This fraction was further separated by preparative GLC (column d, 140 °C) into *n*-butyl iodide and three other components, **21**, **25**, and **16**; retention times (yield) 3.6 (36%), 4.7 (14%), and 8.5 min (28%), respectively. Product **26** was isolated from the residue (1.7 g) by GLC (column d, 195 °C), estimated yield 12%. The following spectral data were obtained.

2-Methyl-1-hexen-3-yne (25).[39,40] ^{1}H NMR (CCl_4) δ 1.17 (t, J = 7.5 Hz, 3 H), 1.8 (s, 3 H), 2.8 (q, J = 7.5 Hz, 2 H), 5.1 (broad s, 2 H); IR (CCl_4) 3100, 2230, 1620, 1370, 890, 840, 695 cm^{-1}; UV λ_{max} (EtOH) 222 (ϵ 6800), 231 sh (5200); mass spectrum m/e (rel intensity) 95 (10), 94 (100), 93 (15), 91 (22), 79 (66), 77 (91), 53 (23), 51 (22), 39 (30).

5,5,6,6-Tetramethyl-3,7-decadiyne (26). ^{1}H NMR (CCl_4) δ 1.1 (t, J = 7.7 Hz, 6 H), 1.2 (s, 12 H), 2.1 (q, J = 7.7 Hz, 4 H); IR (CCl_4) 2980, 1462, 1376, 1365, 1323, 1218 cm^{-1} (no acetylene stretch was observed); mass spectrum m/e (rel intensity) 190 (15), 175 (7), 161 (18), 95 (100), 67 (47), 55 (45); exact mass, 190.1721 (calcd for $C_{14}H_{22}$: 190.1722).

Derivatization of $Me_2C_3Li_2$ with *t*-BuMe$_2$SiCl. To a solution of $Me_2C_3Li_2$, prepared from 30 mmol of 3-methylbutyne, and 50 ml of THF at 0 °C was added 10 g (67 mmol) of *t*-BuMe$_2$SiCl. After 16 h reflux 100 ml of water and 50 ml of hexane were added. The organic phase was separated, washed with two 100-ml portions water, dried ($MgSO_4$), and rotary evaporated to give 9.4 g of crude product. Kugelrohr distillation gave two fractions: 3.2 g, bp 25–60 °C (150 μm) and 4.7 g, bp 60–70 °C (150 μm). By GLC (170 °C, column b) the first fraction was shown to contain 70% of an 8:2 mixture of **19** and **20**. The second fraction contained only **19** and **20**. Retention time (yield) for **19**, 5.3 min (68%) and for **20**, 5.9 min (12%). Preparative isolation of pure allene could not be accomplished on GLC columns a, b, c, or g. Attempted hydrolysis of the acetylene using the procedure of Schmidt and Arens[41] did not work; only recovered allene, acetylene mixture was observed. The following spectral data are for the pure acetylene; the allene data were obtained from a mixture by difference.

1,3-Bis(*tert*-butyldimethylsilyl)-3-methylbutyne (19). ^{1}H NMR (CCl_4) δ 1.20 (s, 6 H), 0.98 (s, 9 H), 0.88 (s, 9 H), 0.03 (broad singlet, 12 H); IR (CCl_4) 2955, 2930, 2885, 2860, 2180, 2150, 1465, 1253, 910, 790 cm^{-1}.

1,1-Bis(*tert*-butyldimethylsilyl-3-methylbuta-1,2-diene (20). ^{1}H NMR (partial) (CCl_4) δ 1.59 (s, allenic methyl); IR for mixture with 19 (neat) 2958, 2938, 2861, 2192, 2150, 1935, 1475, 1465, 1365, 1255sh, 1250, 1010, 859, 835, 822, 808, 787, 775 cm^{-1}. Anal. (mixture of **19** and **20**) Calcd for $C_{17}H_{36}Si_2$: C, 68.92; H, 12.16; Si, 81.92. Found: C, 68.68; H, 12.27; Si, 19.20; mass spectrum (mixture of **19** and **20**) m/e (rel intensity) 296 (4), 239 (14), 166 (11), 155 (22), 151 (11), 125 (10), 124 (8), 123 (4), 115 (5), 99 (16), 97 (6), 83 (4), 74 (8), 73 (100).

References and Notes

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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.

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

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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.

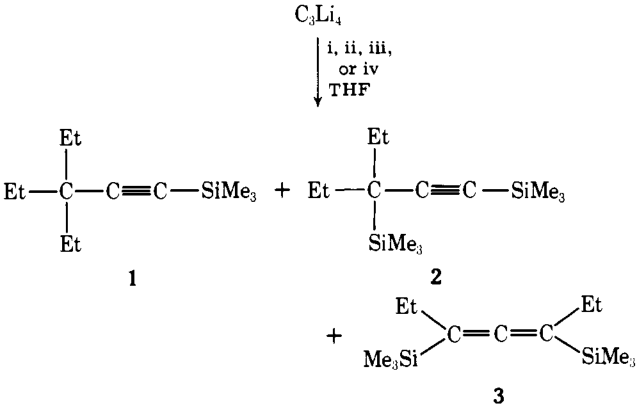
Introduction

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, $[R_2{-}C{=}C{\equiv}C{-}Li]Li$. 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

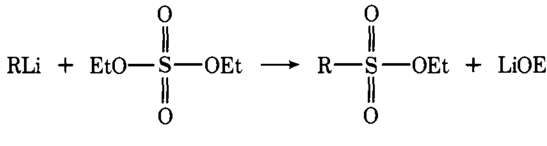
i. 2 equiv $SiMe_3Cl$, 2 h, 0 °C, followed by 2 equiv Et_2SO_4
ii. 3 equiv $SiMe_3Cl$, 2 h, 0 °C, followed by 2 equiv Et_2SO_4
iii. 2 equiv Et_2SO_4, 2 h, 0 °C, followed by 2 equiv $SiMe_3Cl$
iv. added to 10 equiv $Et_2SO_4$and 10 equiv $SiMe_3Cl$

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.

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

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



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