in one batch rather than in THF solution. The ^{19}F signal from the CF_3 group of **11** occurred at 52.3 ppm (benzene solvent, shift relative to fluorobenzene).

Dibromo(pentafluorophenyl)(triphenylphosphine)gold(III) (13). To a suspension of 1.0 g (1.6 mmoles) of pentafluorophenyl(triphenylphosphine)gold in 20 ml of carbon tetrachloride was added dropwise from a syringe 0.255 g (1.6 mmoles) of bromine. Carbon tetrachloride was removed under reduced pressure, and the residue was crystallized twice from ethanol, furnishing 200 mg of product, mp 199–201° dec. From the mother liquor, an additional 150 mg of product was recovered, mp 200° dec. The total yield of product was 350 mg (28%). The mother liquor also yielded 100 mg of a second compound which was recrystallized from acetonitrile and identified as bromo(triphenylphosphine)gold (**14**), mp 248–250° (lit.[49] mp 255.5–256°).

Acknowledgment. We wish to acknowledge with thanks the assistance of Mr. Louis Walther and Dr. Harlan Foster for nmr measurements and Miss Naomi Schlicter for spectral measurements. We are also grateful to Dr. George W. Parshall for helpful discuscussions of the ^{19}F nmr data and to Professor Richard C. Lord for assistance with interpretation of the infrared data.

[49] C. Kowala and J. M. Swan, *Aust. J. Chem.*, **19**, 547 (1966).

Polylithium Compounds. III. Polylithium Compounds from Propyne and 1-Butyne, and Their Polysilicon Derivatives[1,2]

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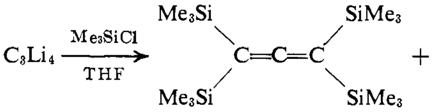
Abstract: Propyne reacts with *n*-butyllithium in hexane to form C_3Li_4, liberating 4 equiv of *n*-butane. With trimethylchlorosilane in tetrahydrofuran, C_3Li_4 gives tetrakis(trimethylsilyl)allene (**1**) in 70% yield along with some 1,3,3-tris(trimethylsilyl)propyne (**2**) and other products. Partial thermal isomerization of **2** to its allenic isomer, 1,3,3-tris(trimethylsilyl)propadiene (**3**), can be effected. 1-Butyne forms a trilithio derivative with 3 equiv of *t*-butyllithium; with trimethylchlorosilane, this produces a mixture of 1,3,3-tris(trimethylsilyl)-1-butyne (**6**) and 1,1,3-tris(trimethylsilyl)-1,2-butadiene (**7**). **6** and **7** are also obtained by lithiation of either **2** or **3** followed by treatment with methyl iodide. The structures of the polylithium compounds in hexane solution have been studied by infrared spectroscopy. They appear to have allenic structures, *e.g.*, $Li_2C{=}C{=}CLi_2$.

In a communication[3] we reported the lithiation of propyne to C_3Li_4 and the reaction of this tetralithio compound with trimethylchlorosilane to form polysilicon derivatives. This paper reports a more complete investigation of the polylithiation of propyne and of 1-butyne, a study of the polysilicon derivatives available from them, and preliminary work on the structure of the polylithium compounds in solution.

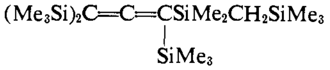
C_3Li_4 is best obtained by adding propyne in hexane solution slowly to a hexane solution of *n*-butyllithium at room temperature, then refluxing the mixture for several hours. When 4 or more equiv of *n*-butyllithium per equivalent of propyne is present, 4 equiv of *n*-butane is liberated, showing that the propyne undergoes essentially complete lithiation to C_3Li_4. The resulting solution reacts vigorously with water to give a gas identified by infrared spectroscopy as propyne, containing some allene. Derivatization with trimethylchlorosilane is best effected by cooling the C_3Li_4 solution to −70° and adding the silyl reagent in tetrahydrofuran solution. Under these conditions the major product is tetrakis(trimethylsilyl)allene (**1**).[4] A trissilyl by-product is also found having exclusively the acetylenic structure **2**, and about 5% of the product is the pentasilicon allene, **4**.



1, 70–75%

$(Me_3Si)_2CH{-}C{\equiv}C{-}SiMe_3$ +

2, 15%



$$(Me_3Si)_2C{=}C{=}\underset{\displaystyle SiMe_3}{\underset{|}{C}}SiMe_2CH_2SiMe_3$$

4, 5%

Both **1** and **2** are colorless oils, stable at room temperature, and **1** is inert to oxygen, water, and dilute acids. When heated under nitrogen at 110°, **2** undergoes partial isomerization into the allene **3**, the limiting composition at this temperature being 60% (**3**)–40% (**2**).

$$\underset{\textbf{2}}{(Me_3Si)_2CHC{\equiv}CSiMe_3} \xrightarrow{110°} \underset{\textbf{3}}{(Me_3Si)_2C{=}C{=}CHSiMe_3}$$

The structures of all of the products were established using ir, nmr, and mass spectroscopy as well as elemental analysis. Compounds **1**, **3**, and **4** all show strong ir bands in the allenic region, near 1900 cm^{-1}, whereas **2** has instead a strong C≡C stretching absorption at 2180 cm^{-1} (Figure 1).[5] Compound **1** shows

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[1] This work was supported in part by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, USAF Grant No. AF-AFOSR-1061-66. Grateful acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support.

[2] Previous paper in this series: R. West and P. C. Jones, *J. Amer. Chem. Soc.*, **90**, 2656 (1968).

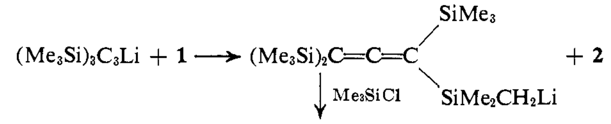
[3] R. West, P. A. Carney, and I. C. Mineo, *ibid.*, **87**, 3788 (1965).

[4] Compound **1** has recently been isolated by interesting *in situ* reaction of trimethylchlorosilane with various complex halogenated hydrocarbons; see D. Ballard and H. Gilman, *J. Organometal. Chem.*, **14**, 87 (1968), and references therein.

[5] (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co., London, 1958, pp 58–62; (b) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 134.

only a single nmr absorption at τ 9.90, whereas **2** and **3** each have three resonances with relative intensity 1:18:9, consistent with the assigned structures. For **4**, ir band at $1050\ \text{cm}^{-1}$[6] and an nmr resonance τ 10.15[7] both indicate the presence of an $SiCH_2Si$ moiety.

Compound **4** probably arises from lithium–hydrogen exchange during derivatization, leading to $-SiCH_2Li$ intermediates. A possible route is



$$(Me_3Si)_3C_3Li + \mathbf{1} \longrightarrow (Me_3Si)_2C{=}C{=}C(SiMe_3)(SiMe_2CH_2Li) + \mathbf{2}$$
$$\downarrow Me_3SiCl$$
$$\mathbf{4}$$

We have shown earlier that methylsilyl protons are unusually acidic and are relatively easily metalated by organolithium compounds.[8]

The results of the derivatization depend greatly on the solvent used. If the reaction with Me_3SiCl is carried out in hexane, the mixture still gives a positive Gilman color test I[9] (indicating organolithium compound to be present) after 16 hr of reflux, and the yield of **1** is less than 10%. With diethyl ether or 1,2-dimethoxyethane present the reaction can eventually be brought to completion (negative Gilman color test), but the yield of **1** is only about 15%. Compound **2** and 1,3-bis(trimethylsilyl)propyne are the major products in these reactions. With tetrahydrofuran the coupling reaction is much faster, and a high yield of **1** is obtained. A basic solvent is apparently necessary to promote coupling with trimethylchlorosilane, as has often been observed for related reactions. With ether or dimethoxyethane, proton abstraction from the solvent apparently competes favorably with coupling, so that most of the C_3Li_4 acquires at least one proton during derivatization. Only with tetrahydrofuran was the coupling reaction rapid enough so that proton abstraction (leading to **2**) became a minor process.

No attempt has yet been made to explore fully the obvious possiblilities of C_3Li_4 as a reagent for synthesis of allenes. However, derivatization with trimethyltin chloride gave a high-boiling liquid as the principal product. This material was unstable at room temperature and was not analyzed, but its spectroscopic properties (allenic $\nu(C{=}C{=}C)$ at $1850\ \text{cm}^{-1}$, singlet proton resonance at τ 9.88) strongly suggest that it is tetrakis(trimethylstannyl)allene, $(Me_3Sn)_2C{=}C{=}C(SnMe_3)_2$.

A remarkable aspect of the derivatization of C_3Li_4 is that the tetrakissilyl derivative is obtained exclusively in the allenic form as **1**, whereas the tris compound is produced as the acetylenic isomer **2**. To study this point we prepared tris(trimethylsilyl)allenyllithium, $(Me_3Si)_3C_3Li$ (**5**), which must be the intermediate present immediately prior to **1**. **5** was obtained by *n*-butyllithium metalation either of **2** or of its isomer **3**. With trimethylchlorosilane in tetrahydrofuran, **5** gives **1** in nearly quantitative yield. Quenching with water converts **5**, again in high yield, to a *mixture* of **2** and **3**. Finally, treatment of **5** with methyl iodide also results in a mixture of two isomers, 1,3,3-tris(trimethylsilyl)-1-butyne (**6**) and 1,1,3-tris(trimethylsilyl)-1,2-butadiene (**7**).

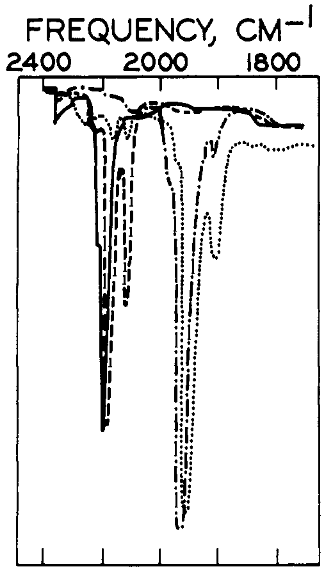
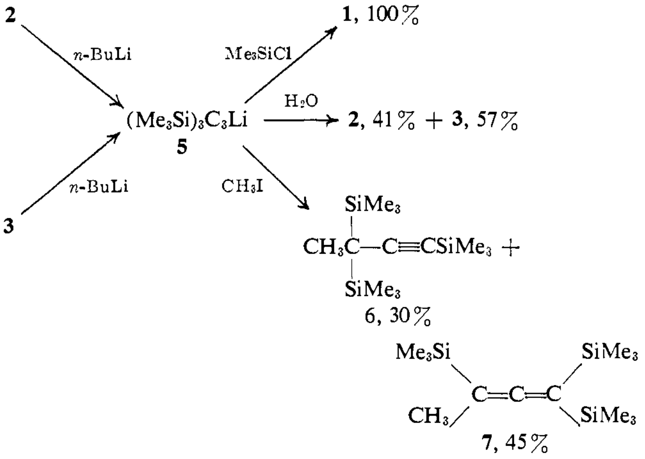


Figure 1. Infrared spectra in the acetylenic and allenic stretching region: ········, **1**; --------, **2**; –·–·–·–·, **3**; ————, $Me_3SiCH_2C{\equiv}CSiMe_3$. Spectra taken on pure liquids between sodium chloride plates.



Compounds **6** and **7** were identified by their spectroscopic properties, which are similar to those of **2** and **3**. These results show that **5** behaves in an ambient fashion undergoing reaction either at the disubstituted position to give acetylenes or at the monosubstituted position to give allenes. The formation of **1** exclusively from **5** is almost surely sterically controlled, for inspection of models shows that compounds with three trimethylsilyl groups attached to a single carbon atom are seriously overcrowded.

Polylithiation of 1-Butyne. While our initial studies were in progress, Eberly and Adams[10] published a note on the formation of a dilithium derivative from excess *n*-butyllithium and 1-butyne, formulated as the *n*-BuLi complex $CH_3CHLiC{\equiv}CLi\cdot n\text{BuLi}$. We find that approximately 2 equiv of *n*-butane is indeed released when 1-butyne reacts with *n*-BuLi at room temperature in

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(6) A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).

(7) Resonance above τ 10.0 is diagnostic for $SiCH_2Si$ protons.

(8) R. West and G. A. Gornowicz, *J. Amer. Chem. Soc.*, **90**, 4478 (1968). In this communication it is shown that trimethylchlorosilane itself undergoes lithiation under favorable conditions to form $Me_2Si(Cl)CH_2Li$ which couples with excess Me_3SiCl to give $Me_3SiCH_2SiMe_2Cl$. The latter intermediate, if formed during derivatization in the propyne reaction, would also lead to formation of **4**. See also D. J. Peterson, *J. Organometal. Chem.*, **9**, 373 (1967).

(9) H. Gilman and H. Yablunky, *J. Amer. Chem. Soc.*, **63**, 839 (1941).

(10) K. C. Eberly and H. E. Adams, *J. Organometal. Chem.*, **3**, 165 (1965).

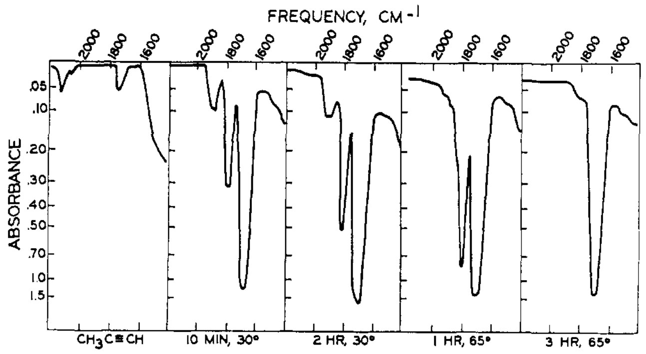

Figure 2. Infrared absorption in the allenic region for propyne (left) and for propyne + 4 *n*-butyllithium in hexane, as a function of time and temperature after addition.

hexane, consistent with the proposed formation of a dilithium derivative. However, when *t*-butyllithium is used instead as the metalating agent, 3 equiv of isobutane is obtained, showing that a trilithio derivative is formed. When the latter is derivatized in the usual way with trimethylchlorosilane, the principal products are the two isomers described above, 1,3,3-tris(trimethylsilyl)-1-butyne (**6**) and 1,1,3-tris(trimethylsilyl)-1,2-butadiene (**7**).

$$\mathrm{CH_3CH_2C{\equiv}CH} \xrightarrow[\text{hexane}]{t\text{-BuLi}} \mathrm{CH_3C_3Li_3} \xrightarrow[\text{THF}]{\mathrm{Me_3SiCl}} \mathbf{6},\ 30\% + \mathbf{7},\ 50\%$$

A small amount of a tetrasilyl compound identified as 1,3,3,4-tetrakis(trimethylsilyl)-1-butyne was also isolated from the reaction mixture. This compound probably arises from lithium–hydrogen exchange occurring during derivatization rather than from a tetralithio species $C_4H_2Li_4$. Increasing the amount of *t*-butyllithium or the reaction time did not increase the yield of the tetrakissilyl compound.

When a "ditlithiobutyne" solution, prepared according to the direction of Eberly and Adams,[10] was treated with trimethylchlorosilane, a mixture of **6** and **7** was again produced, in about 40% yield based on 1-butyne. If the lithiated species present in solution is actually $CH_3CLiHC{\equiv}CLi \cdot C_4H_9Li$ as suggested, further lithiation of the 1-butyne by *n*-butyllithium could take place during derivatization, leading to some **6** and **7**. However, there is no physical evidence for the dilithiobutyne–*n*-butyllithium complex, and the solution could equally well contain a mixture of variously lithiated 1-butynes, with some trilithio derivative already present.

The results with 1-butyne suggest the generalization, now being tested, that all hydrogen atoms on the carbon atom adjacent to the triple bond in 1-alkynes can be replaced by lithium. It is interesting that the presence of one highly acidic proton seems to be important for polylithiation of acetylenes, for under the conditions used for polylithiation of propyne or 1-butyne, 2-butyne was recovered unchanged.[11,12]

Infrared Spectra and Structure of Polylithio Compounds. Few physical methods for structure determination are usable with polylithium compounds such as C_3Li_4, but infrared spectroscopy provides important data. The changes in ir spectrum during the formation of C_3Li_4 were first followed. Figure 2 shows spectra in the most important region (1400–2200 cm⁻¹) as a function of reaction time. Propyne itself shows essentially no absorption between 1600 and 2100 cm⁻¹. After addition of propyne to 4 equiv of *n*-butyllithium in hexane, the solution develops three bands, at 1870, 1770, and 1675 cm⁻¹. The band at 1870 cm⁻¹ grows weaker relative to the other two with time and disappears entirely upon brief heating. Later, with longer refluxing, the band at 1770 cm⁻¹ also weakens and disappears, leaving finally only a single strong band at 1675 cm⁻¹.

None of the bands can be due to $CH_3C{\equiv}CLi$, which shows absorption at 2050 cm⁻¹ and is moreover insoluble in hexane. When propyne is added to only 2 or 3 equiv of *n*-butyllithium, the same three bands are found in the ir spectrum, but the higher frequency bands are proportionately stronger and do not disappear on refluxing.[13] We believe that the three new ir bands, which must represent different species, are due to absorption by $C_3H_2Li_2$, C_3HLi_3, and C_3Li_4, respectively.

Similar metalation studies were carried out on 1,3-bis(trimethylsilyl)propyne and on compound **2**. The ir bands found for all the lithiated derivatives, together with those for the allenes or acetylenes considered in this investigation, are listed in Table I. The acetylenes all show the expected C≡C stretching absorption at high frequency, between 2130 and 2190 cm⁻¹, whereas the allenes all show a C=C=C unsymmetrical absorption below 2000 cm⁻¹. Lithium substitution lowers the stretching frequencies somewhat, so 1-lithiopropyne absorbs 80 cm⁻¹ lower than propyne itself. A much larger shift of 180 cm⁻¹ is found upon going from 1-lithiopropyne to $C_3H_2Li_2$; still further lithium substitution lowers the frequency by 90–100 cm⁻¹ per lithium atom. It seems likely that the large frequency change from C_3H_3Li to $C_3H_2Li_2$ is associated with a structural change from acetylenic to allenic form and that the polylithium derivatives of propyne all have allenic structures in solution. Furthermore, of all the lithium derivatives, only the saltlike $CH_3C{\equiv}CLi$ shows absorption above 2000 cm⁻¹; all the others give absorp-

Table I. Absorption Bands in the 1600–2200-cm⁻¹ Region for Acetylenes, Allenes, and Lithium Compounds in Hexane

Compound	$\nu_{C\equiv C}$, cm⁻¹	$\nu_{C=C=C}$, cm⁻¹
Propyne	2130	
Allene		1970[b]
$CH_3C{\equiv}CSiMe_3$	2190	
$Me_3SiCH_2C{\equiv}CSiMe_3$	2190	
1		1890
2	2185	
3		1900
$CH_3C{\equiv}CLi$	2050[a]	
$C_3HLi(SiMe_3)_2$		1870
$C_3Li(SiMe_3)_3$		1850
$C_3H_2Li_2$		1870
$C_3Li_2(SiMe_3)_2$		1790
C_3HLi_3		1770
C_3Li_4		1675

[a] As a mull in Nujol. [b] T. L. Jacobs and S. Singer, *J. Org. Chem.*, **17**, 475 (1852).

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(11) However, Mulvaney and coworkers have recently shown, and we confirm, that 1-phenylpropyne undergoes lithiation to a trilithio compound.

(12) J. E. Mulvaney, T. L. Falk, and D. J. Newton, *J. Org. Chem.*, **32**, 1674 (1967).

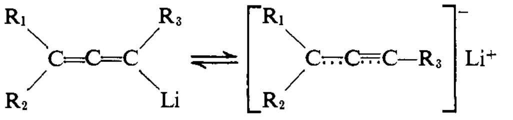
(13) Compound **2** and 1,3-bis(trimethylsilyl)propyne are the major products of trimethylchlorosilane derivatization of such solutions, but some **1** is also formed.

tion below 1900 cm^{-1}. These frequencies seem far too low to be acetylenic, and we therefore believe that the other lithium derivatives $C_3HLi(SiMe_3)_2$, $C_3Li_2(SiMe_3)_2$, and $C_3Li(SiMe_3)_3$ also have allenic structures and should be formulated as $Me_3SiCH{=}C{=}C(Li)SiMe_3$, $Me_3Si(Li)C{=}C{=}C(Li)SiMe_3$, and $(Me_3Si)_2C{=}C{=}C(Li)SiMe_3$, respectively.

The course of lithiation of propyne in hexane should now be considered in the light of the structural evidence. The first step is almost certainly replacement of the acetylenic hydrogen to give 1-lithiopropyne. This must, however, be rapidly metalated to a dilithio derivative, for no precipitate of 1-lithiopropyne is observed if excess butyllithium is present. With the introduction of the second lithium atom,[14] isomerization to the alternate structural form takes place, and the lithium atoms are now bonded to two formally sp^2 π-hybridized carbon atoms. The final two steps, which take place concurrently, involve removal of vinyl hydrogen atoms from the terminal carbon atoms in the allene.

$$\begin{tikzcd}
CH_3C\equiv CH \arrow[r, "n\text{-BuLi}"] & {} & {} \\
CH_3C\equiv CLi \arrow[r, "n\text{-BuLi}"] & LiHC{=}C{=}CHLi \arrow[r, "n\text{-BuLi}"] & Li_2C{=}C{=}CHLi \arrow[d, "n\text{-BuLi}"] \\
& & Li_2C{=}C{=}CLi_2
\end{tikzcd}$$

Although the existence of any high concentration of ions in hexane seems unlikely, our data do not rule out the existence of ionized species in equilibrium with covalent lithium compounds. In ether solvents, in particular, partial ionization to lithium cations and allenyl anions seems reasonable



R_1, R_2, R_3 = Li or Me_3Si

Delocalized allenyl ions of this sort have been proposed by Cram[15] to account for the formation of acetylenic and allenic products from substituted acetylenes and potassium *t*-butoxide in alcohol.[15,16] Similarly, the coupling reactions of our lithium compounds might take place through such ambient anions, accounting nicely for the formation of both allenic and acetylenic products.[17]

Solid C_3Li_4. Although C_3Li_4 is normally stable in hexane solution, slow removal of the solvent sometimes leads to precipitation of an intensely reactive orange-red solid, presumably solid C_3Li_4. When precipitation is complete, the supernatant solvent gives a negative Gilman color test,[9] showing that no organolithium compound is present in solution. The solid gives a strong color test; it inflames in air and reacts violently with water to give mostly propyne. Derivatization of the solid with trimethylchlorosilane in tetrahydrofuran gives the same products as obtained from the hexane solution of C_3Li_4, in about the same proportions.

The precipitated C_3Li_4 will *not* redissolve in excess hexane, even on warming. This suggests that a structural change has taken place, perhaps to an ionic form, and that the hexane solution of C_3Li_4 is only metastable. It is interesting to compare this solid with the unusual magnesium carbide, Mg_2C_3, which also undergoes hydrolysis to give propyne.[18] Mg_2C_3 is known only as a solid and is distinctly unreactive compared to C_3Li_4. For instance, it is inert to bromine in carbon tetrachloride,[19] whereas our C_3Li_4 explodes with bromine. The unreactivity of the magnesium compound appears to be related to its insolubility and high crystal energy. Mg_2C_3 and also solid C_3Li_4 may be derivatives of the unknown ion C_3^{4-}, which is isoelectronic with carbon dioxide and should therefore be linear.

Experimental Section

All reactions involving lithium compounds were carried out in an atmosphere of dry nitrogen. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nmr spectra were recorded on a Varian A-60 spectrometer, using tetramethylsilane as an internal standard in CCl_4 solution. Gas chromatographic separations were made on a Varian Aerograph A-700 chromatograph using columns packed either with SE-30 or QF-1 silicone on Chromosorb W. Mass spectral molecular weights were obtained using a CEC Model 21-101C spectrometer.

The gases propyne and 1-butyne were measured by condensing them into a graduated trap at −78°. 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 side arm of the addition funnel into the butyllithium solution.

Polylithiation of Acetylenes. A. Propyne + 4*n*-Butyllithium. A reaction vessel was fitted with a condenser containing solid carbon dioxide to ensure against loss of the propyne, and a solution of 1.6 g (0.04 mol) of propyne in 10 ml of dry hexane was added *dropwise* to 100 ml of 1.6 *M* *n*-butyllithium in hexane. The addition must be slow, for if it is carried out too rapidly precipitation of hexane-insoluble $CH_3C\equiv CLi$ takes place, making further metalation very difficult. After 1 hr at room temperature, the solid CO_2 condenser was replaced by a water condenser connected to a cold trap for collecting the butane. The reaction mixture was refluxed for 3 hr, after which the solution was bright red and 9.0 g (0.15 mol) of butane had been trapped. No propyne was present in the butane when its purity was checked by gas chromatography.

B. 1-Butyne + 3*t*-Butyllithium. The same experimental technique was used as that reported above for propyne. The reaction mixture consisted of 2.7 g (0.05 mol) of 1-butyne in 100 ml of 1.7 *M* *t*-butyllithium in pentane. After 4 hr of reflux, 8.5 g (0.15 mol) of isobutane had been collected.

C. 1-Butyne + 3*n*-Butyllithium. The same experimental technique was used as that reported above. The reaction mixture consisted of 2.7 g (0.05 mol) of 1-butyne in 100 ml of 1.6 *M* *n*-butyllithium (0.16 mol). After 12 hr of reflux, 5.9 g of butane (0.10 mol) had been collected.

Derivatization with Trimethylchlorosilane. The lithiated acetylene solutions prepared above were cooled to −70° and 35 g (0.32 mol) of Me_3SiCl in 50 ml of freshly distilled tetrahydrofuran was added. The solution was stirred at −70° for 1 hr and then allowed to warm slowly to room temperature. The inorganic salts were filtered off and the product mixtures distilled through a 3-ft Vigreux column. Final separation and purification was effected by gas chromatography.

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(14) Less likely possibilities, not excluded by the data, are (a) that 1-lithiopropyne undergoes isomerization prior to metalation, or (b) that under these conditions propyne is initially metalated in the α position to give 3-lithiopropyne.

(15) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 54, 174, 190, 191.

(16) D. J. Cram, F. Willey, H. P. Fischer, and D. A. Scott, *J. Amer. Chem. Soc.*, **86**, 5370 (1964).

(17) On the other hand we do not feel that ionization is essential to account for the formation of isomeric products in the case of the lithium compounds. A concerted process involving simultaneous loss of lithium and electrophilic attack on the carbon atom remote from the lithium is also reasonable. Moreover, radical pathways for the coupling reaction are conceivable and have not been excluded.

(18) J. F. Cordes and K. Wintersberger, *Z. Naturforsch.*, **12b**, 136 (1957).

(19) W. H. C. Rueggeberg, *J. Amer. Chem. Soc.*, **65**, 602 (1943).

A. **Propyne.** Distillation of the reaction products yielded 1.5 g (15%) of 1,3,3-tris(trimethylsilyl)propyne (**2**), bp 84° (9 mm), 9.1 g (70%) of tetrakis(trimethylsilyl)allene (**1**), bp 117° (9 mm), and 1.5 g (4%) of $(Me_3Si)_2C{=}C{=}C(SiMe_3)SiMe_2CH_2SiMe_3$ (**4**), bp 153° (9 mm). Compound **I** showed the following characteristics: ir spectrum (neat), ν (cm^{-1}) 1890 ($C{=}C{=}C$), 1250 ($SiMe_3$); nmr spectrum (CCl_4, TMS) τ 9.90 (s, $Si\mathit{Me}_3$); mass spectral mol wt, 328.

Anal. Calcd for $C_{15}H_{36}Si_4$: C, 54.77; H, 11.04; Si, 34.19. Found: C, 54.22; H, 11.37; Si, 34.71.

Compound **2** showed the following characteristics: ir spectrum (neat), v (cm^{-1}) 2180, 1000 ($C{\equiv}C$), 1250 ($SiMe_3$); no absorption near 3300 cm^{-1} ($C{\equiv}CH$); nmr (CCl_4, TMS) τ 8.98 (s, 1, CH), 9.90 (s, 18, $Si\mathit{Me}_3$), 9.92 (s, 9, $Si\mathit{Me}_3$); mass spectral mol wt, 256.

Anal. Calcd for $C_{12}H_{28}Si_3$: C, 56.21; H, 11.01; Si, 32.80. Found: C, 56.36; H, 10.88; Si, 32.89.

Compound **4** showed the following characteristics: ir spectrum (neat), ν (cm^{-1}) 1890 ($C{=}C{=}C$), 1250 ($SiMe_3$), 1050 ($SiCH_2Si$);[6] nmr spectrum (CCl_4, TMS) τ 9.88 (s, 6, $Si\mathit{Me}_2$), 9.90 (s, 27, $Si\mathit{Me}_3$), 9.95 (s, 9, $Si\mathit{Me}_3$), 10.15 (s, 2, $Si\mathit{CH}_2Si$); mass spectral mol wt, 400.

Anal. Calcd for $C_{18}H_{44}Si_5$: C, 35.0; H. 11.0; Si, 54.0. Found: C, 35.25; H, 11.28; Si, 53.95.

1-Butyne and *t*-Butyllithium. Distillation of the products yielded 9.5 g (70%) of a mixture of 1,3,3-tris(trimethylsilyl)butyne-1 (6) and 1,1,3-tris(trimethylsilyl)-1,2-butadiene (**7**), bp 95–100° (9 mm). Compounds **6** and **7** could not be separated by gas chromatography for separate analyses, but the combination was analyzed. The compounds were identified by the nmr spectrum of the mixture and of 6 which could be collected approximately 90% pure by successive passes through the gas chromatograph. Integration of the nmr spectrum of the mixture showed 35% 6 and 65% **7**. Compound 6 showed the following characteristics: ir spectrum (neat), v (cm^{-1}) 2160 ($C{\equiv}C$), 1250 ($SiMe_3$); nmr spectrum (CCl_4, TMS) τ 8.85 (s, 1, CH_3), 9.90 (*s*, 6, $Si\mathit{Me}_3$), 9.91 (s, 3, $Si\mathit{Me}_3$). Compound **7** showed the following characteristics: ir spectrum (neat), v (cm^{-1}) 1890 ($C{=}C{=}C$), 1250 ($SiMe_3$); nmr spectrum (CCl_4, TMS) τ 8.35 (s, 1, CH_3), 9.90 (s, 9, $Si\mathit{Me}_3$).

Anal. Calcd for $C_{13}H_{30}Si_3$: C, 57.7; H, 11.1; Si, 31.1. Found: C, 57.83; H, 10.80; Si, 31.33.

C. **1-Butyne and *n*-Butyllithium.** Distillation of the products yielded 5.3 g (40%) of a mixture of 1,3,3-tris(trimethylsilyl)butyne-1 (6) and 1,1,3-tris(trimethylsilyl)-1,2-butadiene (**7**).

Thermal Isomerization of 1,3,3-Tris(trimethylsilyl)propyne (2) to 1,1,3-Tris(trimethylsilyl)allene (3). Two grams of **2** was heated to reflux and the isomerization from **2** to **3** was followed by gas chromatography. After 18 hr there was 30% conversion to the allene; 42 hr, 60% conversion; 66 hr, 60% conversion. Greater than 60% conversion could not be attained. Compound **3** showed the following characteristics: ir spectrum (neat), v (cm^{-1}) 1900, 1100 ($C{=}C{=}C$), 1250 ($SiMe_3$); nmr spectrum (CCl_4, TMS) τ 5.90 (s, 1, CH), 9.90 (s, 18, $Si\mathit{Me}_3$), 9.93 (s, 9, $Si\mathit{Me}_3$); mass spectral mol wt, 256.

Anal. Calcd for $C_{12}H_{28}Si_3$ (**3**): C, 56.21; H, 11.01; Si, 32.80. Found: C, 56.31; H, 11.07; Si, 32.91.

Derivatization of C_3Li_4 with Trimethylchlorosilane—Solvent Dependence. Solutions of C_3Li_4 from 1.6 g (0.04 mol) of propyne and 100 ml of 1.6 *M* *n*-BuLi (0.16 mol) were derivatized with trimethylchlorosilane in hexane, diethyl ether, glyme, and THF. Fifty milliliters of each solvent was added with the trimethylchlorosilane to the C_3Li_4 solution at −70°. The reaction mixture was allowed to warm slowly to room temperature, stirred at 30° for 3 hr, then refluxed until a negative Gilman test I indicated that the coupling reaction was complete. The $(Me_3Si)_2C{=}C{=}C(SiMe_3)_2$ (**1**) in the products was separated by distillation through a 3-ft Vigreux column at reduced pressure (10 Torr). The results are summarized in Table II.

Table II. Solvent Dependence of the Derivatization Reaction

Solvent	Reflux time, hr	Yield of **1**
Hexane	16[a]	1.0 g (8%)
Diethyl ether	12	1.8 g (14%)
Dimethoxyethane	3	2.2 g (17%)
Tetrahydrofuran	0	9.1 g (70%)

[a] Gilman test I still positive, H_2O added.

Derivatization with Trimethylchlorostannane—Propyne. A lithiated propyne solution as prepared above was coooled to −70° and 32 g (0.18 mol) of trimethyltin chloride in 50 ml of dry tetrahydrofuran was added. The mixture was stirred at −70° for 1 hr and then allowed to warm to room temperature. The inorganic salts were removed by filtration in a nitrogen atmosphere and the solvents were distilled from a cold pot under vacuum. The dark brown residue was distilled to give 15 g (60%) of a viscous yellow liquid boiling at 120° (0.025 Torr). Gas chromatographic analysis showed that the product contained approximately 90% of one component. The product reacted rapidly with oxygen to form brown unidentified materials. A sealed tube nmr of a purified sample showed a single peak at τ 9.88. The ir and nmr spectra supported the assignment of the structure of the product as tetrakis(trimethylstannyl)allene.

Lithiation of 1,3,3-Tris(trimethylsilyl)propyne (2). Compound **2**, 4.6 g (0.016 mol), was added to 10 ml of 1.6 *M* *n*-BuLi in hexane and the solution was refluxed for 4 hr. At the end of the reflux period the ir spectrum showed no band at 2180 cm^{-1} ($C{\equiv}C$) but a strong band at 1850 cm^{-1}, characteristic of the lithiated species.

A. **Derivatization with Trimethylchlorosilane.** Trimethylchlorosilane, 3.2 g (0.03 mol), in dry THF was added to the above solution at 0° and the resulting mixture was stirred at room temperature 1 hr. Filtration, followed by distillation, yielded 4.9 g (94%) of tetrakis(trimethylsilyl)allene (**1**).

B. **Derivatization with Methyl Iodide.** Excess methyl iodide was added at 0° to the lithiated **2** prepared above. Filtration and fractional distillation gave 3.5 g (83%) of a mixture of 1,3,3-tris(trimethylsilyl)butyne-1 (6) and 1,1,3-tris(trimethylsilyl)-1,2-butadiene (**7**) in the ratio of 40% 6 to 60% **7**.

C. **Derivatization with Water.** Excess water was added to the lithiated **2** prepared above. After removal of the solvent, nmr analysis of the product mixture showed 41% 1,3,3-tris(trimethylsilyl)propyne (**2**) and 59% 1,1,3-tris(trimethylsilyl)allene (**3**).

Lithiation of 1,1,3-Tris(trimethylsilyl)allene (3). Compound **3**, 2.3 g (8.0 mol), was added to 5 ml of 1.6 *M* *n*-BuLi in hexane and the solution was refluxed for 24 hr. At the end of the reflux period the ir showed a weak band at 1900 cm^{-1} ($C{=}C{=}C$) and a very strong band at 1850 cm^{-1} characteristic of the lithiated species.

A. **Derivatization with Trimethylchlorosilane.** Trimethylchlorosilane, 1.6 g (0.015 mol), in dry tetrahydrofuran was added to the above solution at 0° and the resulting mixture was stirred at room temperature for 1 hr. Filtration, followed by distillation, gave 2.3 g (90%) of tetrakis(trimethylsilyl)allene (**1**) and approximately 0.1 g (15%) of $(Me_3Si)_2C{=}C{=}C(SiMe_3)SiMe_2CH_2SiMe_3$ (**4**).

B. **Derivatization with Water.** Excess water was added to the lithiated **3** prepared above. After removal of the solvent, nmr analysis of the product mixture showed 39% 1,3,3-tris(trimethylsilyl)propyne (**2**) and 61% 1,1,3-tris(trimethylsilyl)allene (**3**).

Infrared Study of Polylithiation of Propyne. A typical reaction between propyne and 4 mol of *n*-BuLi was carried out as described above. Samples were removed at intervals by syringe and were placed in a nitrogen-flushed ir cell. The ir spectrum of the solution was recorded using dry hexane in the reference cell. Immediately after the addition of the propyne was complete three strong bands at 1870, 1770, and 1675 cm^{-1} were present. After 1 hr at room temperature the 1870-cm^{-1} band had decreased and the 1770- and 1765-cm^{-1} bands had increased. After 3 hr at 70° there remained only a single strong band at 1675 cm^{-1}.

Preparation of 1-Trimethylsilylpropyne. Excess propyne, 10 ml (0.16 mol), was distilled into 2 ml of dry hexane at −70°. *n*-BuLi, 75 ml. 1.6 *M* in hexane (0.12 mol) was added dropwise to the propyne solution. The reaction mixture was allowed to warm to room temperature and was stirred at 25° for 1 hr. Trimethylchlorosilane, 25 ml, was added at 0° and the mixture was stirred until Gilman test I was negative. The mixture was washed with water and distilled to give 10.5 g (80%) of 1-trimethylsilylpropyne, bp 98–99° (lit.[20] bp 99–100°).

Lithiation of 1-Trimethylsilylpropyne. 1-Trimethylsilylpropyne, 9.0 g (0.08 mol), was dissolved in 50 ml of dry hexane and 50 ml of 1.6 *M* *n*-BuLi (0.08 mol) was added. During 4 hr at room temperature there was very little change in the ir. After 1 hr of reflux, two new peaks at 1850 and 1760 cm^{-1} were observed in the infrared, but the strongest band was still the $\nu_{C\equiv C}$ 2190 cm^{-1} for the starting material. After overnight reflux, the ir showed two strong broad peaks 1850 and 1760 cm^{-1} along with a much weaker 2190 cm^{-1} band. The assignments for these bands are listed in Table I.

Excess trimethylchlorosilane was added to the reaction mixture and the products were worked up in the usual manner. Gas chromatography of the product mixture demonstrated the presence of

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(20) A. D. Petrov, *Dokl. Akad. Nauk SSSR*, **93**, 293 (1953).

$CH_3C{\equiv}CSiMe_3$, $Me_3SiCH_2C{\equiv}CSiMe_3$, $(Me_3Si)_2CHC{\equiv}CSiMe_3$, and $(Me_3Si)_2C{=}C{=}CHSiMe_3$.

Enough $Me_3SiCH_2C{\equiv}CSiMe_3$ was collected for characterization; nmr resonances at τ 9.88 and 8.50 in the ratio of 9:1.

Anal. Calcd for $C_9H_{20}Si_2$: C, 53.26; H, 10.89; Si, 35.85. Found: C, 53.34; H, 10.83; Si, 35.78.

Lithiation of 1,3-Bis(trimethylsilyl)propyne. To a solution of 1,3-bis(trimethylsilyl)propyne, 1.8 g (0.01 mol), in 10 ml of hexane was added 12.5 ml of 1.6 *M* *n*-BuLi (0.02 mol). The ir spectrum of the solution showed a strong band at 2190 cm^{-1} for the C≡C stretching band of the starting material. After 10 min at room temperature the original C≡C intensity was decreased and new bands appeared at 1850 and 1790 cm^{-1}. After 18 hr, only a single strong band at 1790 cm^{-1} was observed. The assignments for these frequencies are listed in Table I. Derivatization of the final solution with trimethylchlorosilane gave 2.9 g (89%) of **1**.

Electron Spin Resonance of Group IV Organometallic Alkyl Radicals in Solution

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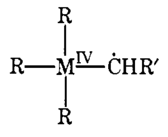
Abstract: Esr spectra have been obtained from a series of alkyl derivatives of group IV metals—silicon, germanium, and tin—by hydrogen abstraction with photochemically generated *t*-butoxy radicals. Abstraction occurs predominantly from the carbon atom α to the metal. In the tetraethyl derivatives, abstraction from the carbon atom β to the metal is also observed. Radicals produced by the latter process have also been observed by addition of trialkylmetal radicals to ethylene. The trends in the coupling constants for these series of α- and β-substituted alkyl radicals are discussed. In the methoxy derivatives of analogous organometallic compounds abstraction occurs from the ethereal methyl group. Line-broadening effects caused by hindered internal rotation are also reported.

Multiple bonding between ligand and the metals of the main group IV elements has been the subject of considerable discussion,[2] and a variety of physical techniques have been brought to bear on this problem. Electron spin resonance (esr) spectra of a number of stable aromatic ion–radical complexes of these metals have been investigated with relation to the possibility of p_π–d_π bonding.[3] Organometallic radicals related to I



$$R_3M^{IV}\!-\!\dot{C}HR'$$

I, R = alkyl, aryl; R′ = H, CH_3; M = group IVB

(particularly M = Si) have also been discussed in an attempt to delineate radical rearrangements in organometallic derivatives analogous to those found in corresponding hydrocarbon radicals.[4a] Heretofore there has been no direct physical evidence for the existence of organometallic radicals of this type in solution.[4b,c]

Experimental Section

Esr spectra were taken with a modified Varian X-band spectrometer utilizing 100-kHz modulation. The microwave bridge was designed around a three-port ferrite circulator. A backward diode (Philco L4154B) was employed as detector in conjunction with a low-noise preamplifier. The magnetic field of a 12-in. magnet was swept by a Varian V3506 magnet flux stabilizer equipped with a modified Varian V3507 slow-sweep unit and was measured by a Harvey-Wells nmr gaussmeter in conjunction with a frequency counter and marker.[5] An unsilvered dewar (fused silica) system of conventional design was used to vary the temperature of the sample. The light source was a water-cooled 2-kW mercury discharge lamp (Pek Labs A-1-B) with an optical system consisting of two fused silica lenses and a spherical mirror. To increase the uv flux at the sample, the optical transmission end plate of a Varian V4531 rectangular cavity was replaced by a similar end plate with wider slots without appreciable loss of *Q*. The preparation and handling of the sample is described elsewhere.[5]

All of the compounds employed in this study were reagent grade commercial samples which were used without further purification. The di-*t*-butyl peroxide was obtained from Wallace and Tiernan Co. and was also used without further purification.

Results and Discussion

We have generated a series of transient organometallic radicals of the general structures I (R = alkyl, R′ = H, CH_3) and the oxygenated analogs II (R, R′ = CH_3, $CH_3CH_2CH_2CH_2$) in solution (ethane, cyclopro-

$$R_n(R'O)_{3-n}MOCH_2\cdot$$

II

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