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

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

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

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

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

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

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

Results and Discussion

Distillation of solvent from a solution of 1-phenylpropyne and 50 equiv of *n*-butyllithium in hexane gives a bright red oil, which upon heating at 75–85° gradually forms a reddish brown slurry, and finally solidifies into a black solid. This solid readily forms a slurry with anhydrous hexane. Slow addition of deuterium oxide to this slurry gives a mixture of deuterated 3- and 1-phenylpropynes in *ca.* 60% yield, both isomers being present in approximately equal amounts. Analysis of these propynes by mass spectroscopy (Table I, run 5) shows the major products to be $C_9D_6H_2$ and $C_9D_5H_3$ along with lesser amounts of C_9D_7H, $C_9D_4H_4$, $C_9D_3H_5$, and even a trace of C_9D_8!

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

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

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

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

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

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(1) This work was supported by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, USAF, Grant No. AF-AFOSR-69-1772.

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

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

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(9) R. West and P. C. Jones, *J. Amer. Chem. Soc.*, **90**, 2656 (1968).

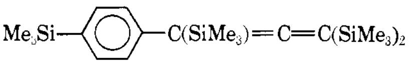
(10) J. E. Mulvaney, T. L. Folk, and D. J. Newton, *J. Org. Chem.*, **32**, 1674 (1967).

Table I. Deuteration of Polylithiated Phenylpropynes

Run	$PhC{\equiv}CCH_3$, *M*	*n*-BuLi	Potentiator, *M*	Solvent	Temp, °C	Time, hr	% phenylpropyne-d_x[a,b] d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
1	0.008	0.08	None	c-C_6H_{12}	81	26			20	32	38	8		
2	0.008	0.08	TMEDA (0.02)	C_6H_{14}	25	26	2	9	56	28	5			
3	0.008	0.08	$KOCMe_2Et$ (0.02)	C_6H_{14}	60	26		6	24	50	18	2		
4	0.008	0.24	None	None	75–85	26		2	9	18	42	25	4	1
5[c]	0.008	0.40	None	None	75–85	48			5	12	36	37	8	1
6	0.008	0.40	None	None	75–85	48		7	17	26	23	19	6	1
7	$PhCH_2C{\equiv}CH$ 0.016	0.16	None	c-C_6H_{12}	81	24		4	18	29	38	8	3	

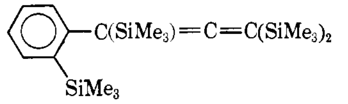
[a] Analyses were made using an ionization potential of 15 eV. Undeuterated 3- and 1-phenylpropynes give parent ions only, no P − 1 peaks being detected under these conditions. Percentages are corrected for P + 1 contributions from ^{13}C. [b] Mixture of 3- and 1-phenylpropynes. [c] Product was not purified by preparative gc.

anism for lithiation of the benzene ring from nucleophilic attack on hydrogen to an electrophilic attack on carbon by the positive lithium, thereby giving only *o*- and *p*-dilithiotoluenes.[9] The group C_3Li_3 probably introduces as much if not more negative charge onto the benzene as does the CH_2Li group. Therefore it is reasonable to expect the fourth lithium atom in the tetralithiophenylallenes to be substituted in the ortho and para positions. This postulate is supported by the isolation of *p*-trimethylsilylphenyltris(trimethylsilyl)allene (**7**). **7** is easily identified by its nmr spectrum, in which



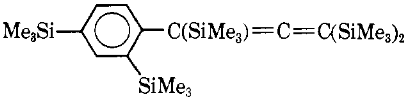
the aromatic protons show the expected AB splitting pattern. Three trimethylsilyl resonances in the ratio 1:1:2 are observed at τ 9.75, 9.78, and 9.82, respectively. The 9.82 resonance is assigned to the two γ trimethylsilyl groups, and the other two absorptions to the indistinguishable para and α trimethylsilyl groups.

Although nmr spectroscopy does not conclusively identify the other tetrasilyl isomer, the spectrum is consistent with the structure *o*-trimethylsilylphenyltris(trimethylsilyl)allene (**8**). A complex pattern is ob-



served for the aromatic protons. Three trimethylsilyl resonances are observed at τ 9.68, 9.82, and 9.93 in the ratio 1:2:1. The 9.68 and 9.82 absorptions are assigned to the ortho and γ trimethylsilyl groups. Interaction between the α and ortho trimethylsilyl groups probably forces the α trimethylsilyl protons over the plane of the benzene ring causing the resonance to shift up to τ 9.93.

The nmr spectrum of the pentasilyl derivative shows a complex pattern for the aromatic hydrogens and four trimethylsilyl resonances at τ 9.68, 9.77, 9.82, and 9.93 in the ratio 1:1:2:1, respectively. This spectrum is quite consistent with the proposed structure *o,p*-bis(trimethylsilyl)phenyltris(trimethylsilyl)allene (**9**). The



para trimethylsilyl group probably absorbs at τ 9.77, compared to 9.75–9.78 for the para trimethylsilyl group of **7**. The ortho group can be assigned to the resonance at τ 9.68, compared to 9.68 for the ortho group in compound **8**. The α trimethylsilyl resonances of **8** and **9** both appear at 9.93.

A mixture of other pentasilyl derivatives, *ca.* equal to the amount of **9**, was also isolated by preparative gc. The components of this mixture could not be separated by gc. Mass spectroscopy showed parent and parent minus methyl peaks at 476 and 461 amu (P calculated for a pentasilyl derivative being 476). The nmr spectrum of this mixture was complex showing at least six MeSi absorptions.

Potentiating agents such as TMEDA and potassium *tert*-amyloxide increase the rate of lithiation of 1-phenylpropyne but give fewer lithium atoms per molecule. One reason for this is that TMEDA is lithiated by the polylithiated phenylpropynes produced.[11] When 1-phenylpropyne was treated with 10 equiv of *n*-butyllithium and 2.5 equiv of TMEDA at room temperature for 3 days, then derivatized with excess trimethylchlorosilane, three major products were obtained: the expected **5** and **7** (see Table III) and the unexpected 3-(*p*-trimethylsilylphenyl)-1,3-bis(trimethylsilyl)propyne (**6**). **6** must be formed in the following manner

$$\begin{array}{l} p\text{-}LiC_6H_4C_3Li_3 + TMEDA \longrightarrow \\ \qquad p\text{-}LiC_6H_4C_3Li_2H + Me(LiCH_2)NCH_2CH_2NMe_2 \\ \qquad \big\downarrow Me_3SiCl \\ \qquad p\text{-}Me_3SiC_6H_4CH(SiMe_3)C{\equiv}CSiMe_3 \\ \qquad \quad \mathbf{6} \end{array}$$

When 1-phenylpropyne is treated with 3 equiv of *n*-butyllithium and 0.75 equiv of TMEDA for only 15 min and then quenched with trimethylchlorosilane only **5** and the disilylated compound **3** are formed, no trace of **6** being detected by gc. **6** is not formed when 1-phenylpropyne is lithiated in the absence of TMEDA either.

3-Phenylpropyne is polylithiated to about the same extent as 1-phenylpropyne (Table I). This is to be expected because 1-phenylpropyne when lithiated in the methyl group immediately rearranges to give the more stable lithium acetylide, 1-lithio-3-phenylpropyne[7] (eq 1). Therefore the same polylithium compounds must be obtained from either 3- or 1-phenylpropyne.

Infrared Spectra and Structures of Polylithium Compounds. In order to determine the structures of the

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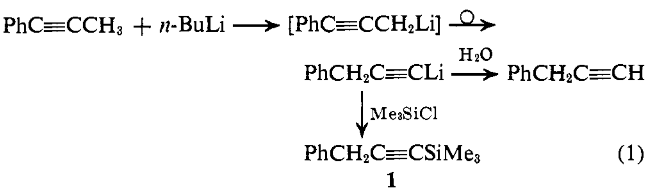
(11) Polylithiated toluenes also metalate TMEDA decreasing the extent of lithiation.[9]



$$\begin{array}{l} PhC{\equiv}CCH_3 + n\text{-}BuLi \longrightarrow [PhC{\equiv}CCH_2Li] \xrightarrow{\bigcirc} \\ \qquad PhCH_2C{\equiv}CLi \xrightarrow{H_2O} PhCH_2C{\equiv}CH \\ \qquad \Big\downarrow Me_3SiCl \\ \qquad PhCH_2C{\equiv}CSiMe_3 \\ \qquad \mathbf{1} \end{array} \qquad (1)$$

intermediate organolithium compounds, 1-phenylpropyne was metalated with 4 equiv of *n*-butyllithium in refluxing cyclohexane. After 1 hr, analysis by nmr showed only unreacted propyne, no absorptions being observed for lithiated phenylpropynes or allenes in the region of τ 2–12 (possibly the polylithium compounds were in suspension). Infrared showed only an intense absorption at 1775 cm^{-1}, arising from a trilithioallene. Gradually this ir absorption became much stronger and the absorptions in the nmr spectrum due to 1-phenylpropyne became weaker. Apparently the introduction of the first lithium atom is much slower than subsequent lithiations, so mono- and dilithiated species are not observed in the ir.

It is possible to prepare the mono- and dilithio compounds, however, by lithiating 3-phenylpropyne. When *n*-butyllithium is added to 10 equiv of 3-phenylpropyne a white solid, 1-lithio-3-phenylpropyne, is formed. It shows only a weak absorption at 2050 cm^{-1} in the 1600–2200-cm^{-1} region of the ir spectrum. Derivatizing with trimethylchlorosilane gives **1**. 3-Phenylpropyne and 2 equiv of *n*-butyllithium give a yellow solid having an intense allenic absorption at 1900 cm^{-1}. Quenching this solid with trimethylchlorosilane gives predominantly **3**. 3-Phenylpropyne and 3 equiv of *n*-butyllithium in cyclohexane give a deep red solution, which exhibits a strong band at 1900 cm^{-1} and a weak band at 1780 cm^{-1} in the ir. This solution probably is a soluble complex of 1-phenyl-1,3-dilithioallene and *n*-butyllithium. Gradually the 1900-cm^{-1} absorption disappears leaving only an intense absorption due to phenyltrilithioallene at 1780 cm^{-1}.

Even though the infrared spectrum shows the dilithium derivative of 3-phenylpropyne to be an allene, quenching with trimethylchlorosilane yields only acetylene **3**, no 1-phenyl-1,3-bis(trimethylsilyl)allene (**4**) being detected either by ir or gc

$$Ph(Li)C{=}C{=}CHLi \xrightarrow{Me_3SiCl} \underset{\mathbf{3}}{Ph(Me_3Si)CHC{\equiv}CSiMe_3}$$

However, the expected **4** is obtained when the monolithium derivatives of **3** are hydrolyzed

$$PhC_3(Me_3Si)_2Li \xrightarrow{H_2O} \underset{\mathbf{4},\ 50\%}{Ph(Me_3Si)C{=}C{=}CHSiMe_3} + \underset{\mathbf{3},\ 50\%}{Ph(Me_3Si)CHC{\equiv}CSiMe_3}$$

Similarly, hydrolysis of 1-phenyl-3-trimethylsilyl-1,3-dilithioallene produces a mixture of **1** and 1-phenyl-3-trimethylsilylallene (**2**)

$$Ph(Li)C{=}C{=}C(SiMe_3)Li \xrightarrow{H_2O} \underset{\mathbf{2},\ 35\%}{PhCH{=}C{=}CHSiMe_3} + \underset{\mathbf{1},\ 65\%}{PhCH_2C{\equiv}CSiMe_3}$$

The lithium derivatives of **1** and **3** are quite interesting. The mono- and dilithium compounds from **1** have only allenic absorptions at 1870 and 1790 cm^{-1}, respectively. However, the infrared spectra of the monolithium derivative of **3** show both acetylenic and allenic absorptions, at 2000 and 1850 cm^{-1}. These bands do not change with time and are probably due to the compounds $Ph(Me_3Si)CLiC{\equiv}CSiMe_3$ and $Ph(Me_3Si)C{=}C{=}C(SiMe_3)Li$. The acetylenic isomer must be stabilized by a combination of delocalization of charge onto the benzene ring and the strong acidifying effect of silicon. When phenyl is replaced by hydrogen or another trimethylsilyl group the organolithium compounds exist only as allenes. Similarly, when the trimethylsilyl group is replaced by hydrogen the organolithium compounds show only allenic absorptions (Table II).

Table II. Absorption Bands in the 1600–2200-cm^{-1} Region for Lithiated Acetylenes and Allenes

Compd	$\nu_{C\equiv C}$, cm^{-1}	$\nu_{C=C=C}$, cm^{-1}
Monolithio		
$CH_3C{\equiv}CLi$[a]	2050	
$PhCH_2C{\equiv}CLi$	2050	
$PhC_3(SiMe_3)_2Li$	2000	1850
$PhC_3H(SiMe_3)Li$		1870
$C_3H(SiMe_3)_2Li$[a]		1870
$C_3(SiMe_3)_3Li$[a]		1850
$CH_2{=}C{=}CHLi$[b]		1890
Dilithio		
$C_3H_2Li_2$[a]		1870
$C_3(SiMe_3)_2Li_2$[a]		1790
PhC_3HLi_2		1900
$PhC_3(SiMe_3)Li_2$		1790
Trilithio		
C_3HLi_3[a]		1770
PhC_3Li_3		1790
$C_3(SiMe_3)Li_3$[a]		1770
Tetralithio		
C_3Li_4[a]		1675

[a] Values reported in ref 4. [b] Value reported in ref 12.

The infrared stretching bands of these polylithiated phenylallenes and acetylenes are very similar to those reported for polylithiated propynes and butynes (Table II). Monolithium compounds from terminal acetylenes have only weak absorptions at 2050 cm^{-1} and all exist as the stable lithium acetylides. Monolithium derivatives of nonterminal acetylenes may exist in either acetylenic or allenic forms having absorptions in the infrared at 2000 and 1850–1870 cm^{-1}, respectively. Allenyllithium[12] absorbs at 1890 cm^{-1}. Dilithium compounds show only allenic absorptions in the range 1790–1900 cm^{-1}. Trilithiated allenes absorb at 1770–1790 cm^{-1} and tetralithioallene at 1675 cm^{-1}. As noted previously,[4] both trimethylsilyl groups and lithium atoms shift the absorption of acetylenes and allenes to lower frequencies.

Experimental Section

All reactions involving organolithium compounds were carried out in an atmosphere of dry nitrogen. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or Schwartzkopf Microanalytical Laboratory, Woodside, N. Y. ^1H nmr spectra were recorded on a Varian A-60 spectrometer. Gas chromatographic separations were made on a Varian Aerograph A-700 chromatograph using columns packed with SE-30 silicone on Chromosorb W. Mass spectral analyses were obtained on an AEI Model MS-9 spectrometer. Infrared spectra were recorded on Perkin-

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(12) F. Jaffe, *J. Organometal. Chem.*, 23, 53 (1970).

Table III. Characterization of Products

No.	Compd[a]	Bp, °C (Torr)	n^tD	Infrared,[b] cm^{-1}	Nmr[c] τ CCl$_4$, TMS	Calcd, %			Found, %		
						C	H	Si	C	H	Si
1	$\mathrm{PhCH_2C{\equiv}CSi}$	65–70 (1)	n^{23}D 1.5045	2180 (C≡C)	2.75 (s, 5, Ar) 6.44 (s, 2, CH$_2$) 9.82 (s, 9, Si)	76.5	8.6	14.9	76.7	8.4	14.7
2	$\mathrm{PhCH{=}C{=}CHSi}$			1925 (C=C=C)	2.85 (s, 5, Ar) 4.18 (d, 1, =CH) 4.65 (d, 1, =CH) 9.85 (s, 9, Si)	76.5	8.6	14.9	76.3	8.5	14.7
3	$\mathrm{Ph(Si)CHC{\equiv}CSi}$	135–140 (10)	n^{22}D 1.4985	2160 (C≡C)	3.75 (s, 5, Ar) 7.18 (s, 1, CH) 9.84 (s, 9, Si) 9.97 (s, 9, Si)	69.2	9.3	21.5	68.0	9.2	21.0
4	$\mathrm{Ph(Si)C{=}C{=}CHSi}$			1900 (C=C=C)	2.81 (s, 5, Ar) 5.20 (s, 1, =CH) 9.77 (s, 9, Si) 9.85 (s, 9, Si)	69.2	9.3	21.5	68.0	9.1	20.6
5	$\mathrm{Ph(Si)C{=}C{=}C(Si)_2}$	120–125 (1)	n^{22}D 1.5230	1880 (C=C=C)	2.90 (s, 5, Ar) 9.80 (s, 9, Si) 9.83 (s, 18, Si)	65.0	9.6	25.3	64.3	9.6	24.3
6	p-$\mathrm{SiC_6H_4(Si)CHC{\equiv}CSi}$			2160 (C≡C)	2.62 (d, 2, Ar) 3.00 (d, 2, Ar) 9.77 (s, 9, Si) 9.82 (s, 9, Si) 9.95 (s, 9, Si)	65.0	9.6	25.3	64.4	9.8	24.0
7	p-$\mathrm{SiC_6H_4(Si)C{=}C{=}CSi_2}$		n^{23}D 1.5230	1875 (C=C=C)	2.65 (d, 2, Ar) 2.87 (d, 2, Ar) 9.75 (s, 9, Si) 9.78 (s, 9, Si) 9.82 (s, 18, Si)	62.3	9.9	27.8	62.3	10.1	28.6
8	o-$\mathrm{SiC_6H_4(Si)C{=}C{=}CSi_2}$			1875 (C=C=C)	2.7 (c, 4, Ar) 9.68 (s, 9, Si) 9.82 (s, 18, Si) 9.93 (s, 9, Si)	62.3	9.9	27.8	62.4	10.2	27.5
9	o,p-$\mathrm{Si_2C_6H_3(Si)C{=}C{=}C(Si)_2}$		n^{23}D 1.5248	1875 (C=C=C)	2.6 (c, 3, Ar) 9.68 (s, 9, Si) 9.77 (s, 9, Si) 9.82 (s, 18, Si) 9.93 (s, 9, Si)	60.4	10.1	29.4	61.0	10.4	28.4

[a] Si = Me$_3$Si–. [b] Neat. [c] s = singlet, d = doublet, c = complex.

Elmer Model 237 and Model 457 spectrometers. All products were purified by preparative gc prior to characterization.

1-Phenylpropyne was used as obtained from Farchan Research Laboratories. *n*-Butyllithium in hexane or cyclohexane was purchased from Foote Mineral Co. Trimethylchlorosilane, Dow Corning Corp., was distilled before use. Deuterium oxide (99.9%) was purchased from Columbia Organic Chemicals, Inc.

3-Phenylpropyne was prepared by adding 200 ml of 1.6 *M* *n*-butyllithium in hexane to a solution of 20 ml (0.16 mol) of 1-phenylpropyne and 10 ml (0.08 mol) of TMEDA. The reaction was quenched with 50 ml of water. The organic phase was washed with two 50-ml portions of 3 *N* hydrochloric acid and two 100-ml portions of water, dried with calcium sulfate, and distilled to give 16 g (88%) of 3-phenylpropyne: bp 75–80° (20 Torr), n^{21}D 1.5225 (lit.[13] bp 68–69° (17 Torr), n^{20}D 1.509).

Metalation of 1- and 3-Phenylpropynes. 1. Derivatization with Deuterium Oxide. Either 1- or 3-phenylpropyne was treated with *n*-butyllithium under the conditions given in Table I. Reactions were quenched by slowly adding excess deuterium oxide to the organolithium mixture, keeping the reaction flask immersed in an ice–water bath. After a negative Gilman test was obtained, lithium deuteroxide was removed by filtration. Distillation of the filtrates gave mixtures of 1- and 3-phenylpropynes (amount of 1-phenylpropyne varying from *ca.* 5 to 50%), bp 65–75° (13 mm), in 50–80% yields. No hydrogen–deuterium exchange occurred during quenching but a small amount of hydrogen–deuterium exchange occurred when the samples were purified by preparative gc. The amount of butane evolved prior to derivatization could not be used as a measure of metalation because all metalations were run under conditions where *n*-butyllithium either decomposed thermally or attacked the potentiating agent.

In a typical experiment, hexane was distilled from a solution of 1 ml (0.008 mol) of 1-phenylpropyne and 250 ml of 1.6 *M* *n*-butyllithium solution to give a bright red oil. This oil was then heated for 48 hr, in an oil bath, at 75–85°. Gradually the oil turned to a black solid. This solid was slurried with 100 ml of anhydrous hexane, cooled with an ice–water bath, and quenched with 15 ml (0.75 mol) of deuterium oxide. Lithium deuteroxide was filtered. Distillation of the filtrate gave 0.6 g (60%) of a mixture of deuterated 3- and 1-phenylpropynes, *ca.* equal amount of each. These propynes were analyzed by mass spectroscopy at an ionizing voltage of 15 eV. Results are given in Table I, run 5.

2. Derivatization with Trimethylchlorosilane. A. Tetrakis- and Pentakis(trimethylsilyl)phenylallenes. Hexane was distilled from a solution of 1 ml (0.008 mol) of 1-phenylpropyne and 150 ml of 1.6 *M* *n*-butyllithium solution. The residue was heated at 75–85° for 48 hr, cooled in a Dry Ice–acetone bath, and quenched with 32 ml (0.25 mol) of trimethylchlorosilane in 100 ml of THF. No reaction was observed until the temperature was raised to 0°. After 5 hr at 0°, a negative Gilman test was obtained. The mixture was added to 200 ml of water. The organic phase was separated, washed with 200 ml of water, dried with CaSO$_4$, and distilled giving 2.5 g (*ca.* 60% yield) of black oil, bp 75–175° (0.2 Torr). Gc showed this material to be a mixture of polysilylated phenylallenes (area per cent): phenyltris(trimethylsilyl)allene (**5**) (16%), *p*-trimethylsilylphenyltris(trimethylsilyl)allene (**7**) (19%), *o*-trimethylsilylphenyltris(trimethylsilyl)allene (**8**) (18%), *o,p*-bis(trimethylsilyl)phenyltris(trimethylsilyl)allene (**9**) (25%), and a mixture of pentakis(trimethylsilyl)phenylallenes, $\mathrm{(Me_3Si)_5C_9H_3}$ (22%). Compounds **7**, **8**, and **9** were isolated pure by preparative gc and characterized (Table III). Compound **5** was identified by comparing its gc retention time with that of an authentic sample. Nmr of the $\mathrm{(Me_3Si)_5C_9H_3}$ mixture shows complex aromatic absorptions at τ 2.7 and at least six trimethylsilyl resonances between τ 9.65 and 9.92. Molecular weight by mass spectroscopy is 476 (calcd 476). This material could not be further purified.

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(13) M. L. Bert and L. C. Dorier, *Bull. Soc. Chim. Fr.*, **39**, 1610 (1926).

B. 3-Phenyl-1-trimethylsilylpropyne (1). A solution of 25 ml of 1.6 *M* *n*-butyllithium in hexane was added to 5 ml (0.04 mol) of 1-phenylpropyne and 1.4 ml (0.01 mol) of TMEDA. The mixture was heated at reflux for 20 min, cooled to −78°, and quenched with 7.5 ml (0.06 mol) of trimethylchlorosilane in 25 ml of THF. The product was added to 50 ml of water. The organic phase was separated, washed with two 25-ml portions of water, and distilled giving 3.5 g (50%) of **1** and 2.2 g of a mixture of **1** and **3**. See Table III for physical properties of **1**.

C. 3-Phenyl-1,3-bis(trimethylsilyl)propyne (3). In the same manner described for **1**, 5 ml (0.04 mol) of 1-phenylpropyne was treated with 2.8 ml (0.02 mol) of TMEDA and 50 ml of 1.6 *M* *n*-butyllithium (0.08 mol) in hexane giving 7.2 g of a mixture of **1** (15%), **3** (70%), and **5** (15%) (gc area per cent), bp 80–120° (1 Torr). **3** was isolated from **1** and **5** by preparative gc and characterized (Table III).

D. Phenyltris(trimethylsilyl)allene (5). As above, metalation of 1-phenylpropyne (5.0 ml, 0.04 mol) with 3.2 ml (0.03 mol) of TMEDA and 75 ml of 1.6 *M* *n*-butyllithium in hexane followed by derivatization with 20 ml (0.16 mol) of trimethylchlorosilane in 75 ml of THF gave 10 g of a mixture of **5** and **3**, ratio 3:1, bp 95–125° (1 Torr). **5** was isolated pure by gc and characterized (Table III). Estimated yield of **5** was about 60%.

E. 3-(*p*-Trimethylsilylphenyl)-1,3-bis(trimethylsilyl)propyne (6). A mixture of 2 ml (0.016 mol) of 1-phenylpropyne, 5.5 ml (0.40 mol) of TMEDA, and 100 ml of 1.6 *M* *n*-butyllithium in hexane was stirred at room temperature for 3 days. Derivatization with 25 ml (0.20 mol) of trimethylchlorosilane in 100 ml of THF at −78° followed by an aqueous work-up gave 4.3 g of oil, bp 150–165° (1.5 Torr). Gc showed this oil to be a mixture of **5** (20%), **6** (20%), and **7** (60%). **6** was isolated by preparative gc and characterized (Table III).

F. 1-Phenyl-3-trimethylsilylallene (2). A solution of 1.8 g (0.01 mol) of 3-phenyl-1-trimethylsilylpropyne (**1**) and 14 ml of 1.6 *M* *n*-butyllithium in hexane was heated at reflux for 30 min to give a yellow solid. The mixture was added to 75 ml of 6 *N* hydrochloric acid. The organic phase was separated and concentrated. Gc showed only **1** and **2** to be present in the ratio 2:1. Allene **2** was isolated by preparative gc and characterized (Table III).

G. 1-Phenyl-1,3-bis(trimethylsilyl)allene (4). A solution of 3.5 g (0.013 mol) of 3-phenyl-1,3-bis(trimethylsilyl)propyne (**3**) and 10 ml of 1.6 *M* *n*-butyllithium in hexane was heated at reflux for 30 min, then added to 25 ml of 6 *N* hydrochloric acid. The organic phase was separated and concentrated to give an equimolar mixture of **3** and **4**. Compound **4** was isolated by preparative gc and characterized (Table III).

3. Infrared Spectra of Lithiated Phenylpropynes and -allenes. A. 1-Lithio-3-phenylpropyne. Addition of a solution of 1 ml of 1.6 *M* *n*-butyllithium in cyclohexane to 2 ml (16 mmol) of 3-phenylpropyne gave a reddish white solid. The solid was filtered under nitrogen and washed with three 1-ml portions of cyclohexane. The ir spectrum (Nujol) of the solid shows only a weak absorption at 2050 $\mathrm{cm^{-1}}$ in the region 1600–2200 $\mathrm{cm^{-1}}$. Quenching with trimethylchlorosilane gives predominately **1**.

B. 1-Phenyl-1,3-dilithioallene. Addition of a solution of 0.1 ml (0.8 mmol) of 3-phenylpropyne in 1 ml of cyclohexane to a solution of 1 ml of 1.6 *M* *n*-butyllithium in cyclohexane gave a yellow solid. This solid was isolated as described above. The ir spectrum (Nujol) showed a very strong band at 1900 $\mathrm{cm^{-1}}$. Derivatization of the solid with trimethylchlorosilane gives predominantly **3**.

C. Phenyltrilithioallene. A solution of 0.2 ml (1.6 mmol) of 3-phenylpropyne in 1 ml of cyclohexane was added to 3.3 ml of 1.6 *M* *n*-butyllithium in cyclohexane. Immediately after mixing, ir analysis of the deep red solution showed a very strong band at 1900 $\mathrm{cm^{-1}}$, $\mathrm{Ph(Li)C{=}C{=}CHLi}$, and a weak band at 1780 $\mathrm{cm^{-1}}$, $\mathrm{Ph(Li)C{=}C{=}CLi_2}$. Gradually the 1900-$\mathrm{cm^{-1}}$ band disappeared and the 1780-$\mathrm{cm^{-1}}$ band became very strong.

D. Lithium Derivatives of 3-Phenyl-1-trimethylsilylpropyne (1). A solution of 0.2 g (1 mmol) of **1**, 2 ml of cyclohexane, and 0.6 ml of 1.6 *M* *n*-butyllithium in cyclohexane was heated briefly at reflux. The ir spectrum showed a weak band due to **1** at 2190 $\mathrm{cm^{-1}}$, a strong broad absorption assigned to $\mathrm{Ph(Li)C{=}C{=}CHSiMe_3}$ at 1870 $\mathrm{cm^{-1}}$, and a weak band at 1790 $\mathrm{cm^{-1}}$ assigned to $\mathrm{Ph(Li)C{=}C{=}C(SiMe_3)Li}$. Another 1 ml of 1.6 *M* *n*-butyllithium solution was added. With time the 1870-$\mathrm{cm^{-1}}$ band became weaker and the 1790-$\mathrm{cm^{-1}}$ band grew stronger.

E. Lithium Derivatives of 3-Phenyl-1,3-bis(trimethylsilyl)propyne (3). A solution of 0.5 g (1.9 mmol) of **3**, 2 ml of cyclohexane, and 1.5 ml of 1.6 *M* *n*-butyllithium in cyclohexane was heated to reflux, cooled, and analyzed by ir spectrum showing two strong absorptions at 2000 and 1850 $\mathrm{cm^{-1}}$ of about equal intensity. These bands did not change with time. The 2000-$\mathrm{cm^{-1}}$ band is attributed to the species 3-phenyl-1,3-bis(trimethylsilyl)-3-lithiopropyne, $\mathrm{Ph(Me_3Si)LiCC{\equiv}CSiMe_3}$, and the 1850-$\mathrm{cm^{-1}}$ band to the species 1-phenyl-1,3-bis(trimethylsilyl)-3-lithioallene, $\mathrm{Ph(Me_3Si)C{=}C{=}C(SiMe_3)Li}$.

A New Synthesis of α,β-Unsaturated Aldehydes Using 1,3-Bis(methylthio)allyllithium

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Abstract: Reaction of 1,3-bis(methylthio)-2-methoxypropane (**5**) (easily available in two steps from epichlorohydrin) with lithium diisopropylamide in tetrahydrofuran produces the lithio derivative of the 1,3-bis(methylthio)-allyl anion (**1**). The reagent **1** so generated has been shown to serve effectively as the equivalent of the unknown β-formylvinyl anion by the synthesis of a number of α,β-unsaturated aldehydes starting with alkyl halides, carbonyl compounds, or 1,2-epoxides. In the case of the last two substrates a trifunctional γ- or δ-hydroxy α,β-unsaturated aldehyde unit results. This is a unique and useful feature of the new method which has been exploited in a total synthesis of prostaglandin $\mathrm{F_{2\alpha}}$. It is concluded from these studies that the use of the reagent **1** represents a significant new approach to the synthesis of conjugated aldehydes which should be advantageous in a wide range of synthetic problems.

The β-carbon atom of the unit –CH=CHCHO is a receptor for nucleophiles and free radicals, but not for electrophiles. The present paper reports a reagent which functions as the equivalent of this unit having inverted, *i.e.*, nucleophilic, reactivity. This inversion imparts a special applicability and utility in organic synthesis,(1) as is illustrated by a number of test cases.

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(1) For a discussion of other examples of the synthetic strategy of group equivalents having inverted reactivity, see (a) E. J. Corey, *Pure*