

## HEXAKIS(TRIMETHYLSILYL)-2-BUTYNE BY TRIMETHYLSILYLATION OF HEXACHLORO-1,3-BUTADIENE

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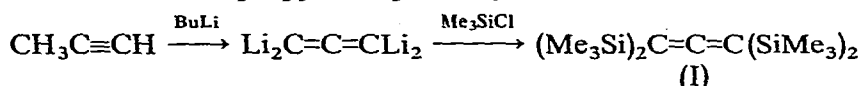
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### SUMMARY

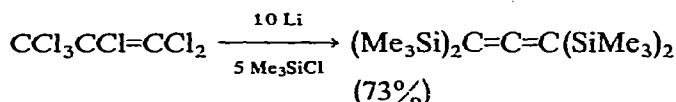
Lithium (or sodium) chlorotrimethylsilane and hexachlorobutadiene in THF give hexakis(trimethylsilyl)-2-butyne in good yields. Some chemical properties of this sterically hindered compound are described. In contrast, magnesium under similar conditions gives bis(trimethylsilyl)butadiyne; whereas barium fails to react.

The search for suitable thermally stable polymers has led to the study and preparation of new organosilicon compounds, particularly those containing functional groups (e.g. Si-H, Si-Cl)<sup>1-4\*</sup>. Incidental to this study we have also prepared a number of carbofunctional organosilicon compounds, mainly those containing olefinic, acetylenic and allenic linkages<sup>3,5-8</sup>.

The production of tetrakis(trimethylsilyl)allene (I) from the metalation of propyne by *n*-butyllithium followed by derivatization with chlorotrimethylsilane was first described by West and co-workers<sup>9</sup>. The organometallic intermediate, previously thought to be tetralithiopropyne, is probably tetralithioallene<sup>10</sup>. The allene (I) has



since been made, in a variety of yields, from a wide spectrum of polyhalogenated compounds (aromatic, aliphatic and heterocyclic), lithium (or magnesium) and chlorotrimethylsilane<sup>1,5-8</sup>. The highest yield was obtained in the following reaction:

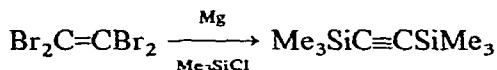


This reaction seems to be general for the synthesis of silylated allenes and we have obtained tetrakis(dimethylsilyl)-, tetrakis(methylphenylsilyl)- and tetrakis(diphenylsilyl)allene in a similar fashion from magnesium, the appropriate chlorosilane and hexachloropropene<sup>11</sup>.

This type of *in situ* Grignard or organolithium reaction represents an extension of the methods that previous workers have used to prepare polytrimethylsilylated

\* See also previous papers in the series "Polyhalo-organometallic and -organometalloidal compounds.

products from halogenated methanes and ethylenes<sup>12,13</sup>. Bis(trimethylsilyl)acetylene is formed in high yield by this method from an excess of magnesium, chlorotrimethylsilane and tetrabromoethylene<sup>12</sup>, and we have observed a similar reaction using lithium, chlorotrimethylsilane and tetrachloroethylene.



The high yields and the selective character of these reactions (particularly with lithium) have prompted us to undertake a study of more complicated aliphatic chlorocarbons.

Recent literature<sup>14</sup> has clearly shown the relative chemical inertness of hexachloro-1,3-butadiene (II). We have reacted hexachlorobutadiene with a number of metals and chlorotrimethylsilane in THF (see Table 1).

TABLE I

INTERACTION OF HEXACHLOROBUTADIENE WITH METALS AND CHLOROTRIMETHYLSILANE IN THF

Metal	Product <sup>a</sup>	Yield (%)	Other Products (%)
Li	$\text{R}_3\text{C}-\text{C}\equiv\text{C}-\text{CR}_3$	40	$\text{R}_2\text{C}=\text{C}=\text{CR}_2$ (0-5)
Na	$\cdot\text{R}_3\text{C}-\text{C}\equiv\text{C}-\text{CR}_3$	25	Traces of acetylenes, allenes and olefins
Mg	$\text{RC}\equiv\text{C}-\text{C}\equiv\text{CR}$	44	At least 21 other products
Ba			Little or no reaction

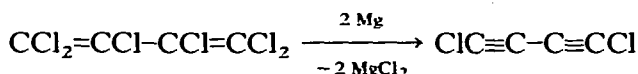
<sup>a</sup> R = SiMe<sub>3</sub>

Choice of solvent is a pertinent factor in these reactions. Similar experiments using other solvents gave reduced yields or no reaction. 1,2-Dimethoxyethane, tetrahydropyran and tetrahydro-2-methylfuran gave lower yields of hexakis(trimethylsilyl)-2-butyne (III) using lithium; whereas with 2,2,4,4-tetramethyltetrahydrofuran, diethyl ether or 1,4-dioxane no appreciable reaction occurred using either lithium or magnesium.

In an effort to learn something of the reaction pattern leading to the formation of hexakis(trimethylsilyl)-2-butyne (III) and bis(trimethylsilyl)butadiyne (IV) we have reacted lithium and magnesium with II in THF at room temperature. Subsequent to a vigorous reaction chlorotrimethylsilane was added after removal of unreacted metal when vapor phase chromatography showed none of II present. The product of the reaction was a black insoluble carbonaceous-like material containing a little chlorine and traces of silicon. A related reaction but without adding chlorotrimethylsilane to derivatize any intermediate present gave a similar blackish product. In neither experiment was any III or IV obtained. The black material, transparent in the infrared region (650-5000 cm<sup>-1</sup>) did not melt at 500°. The production of this carbon-like substance could be attributed to reduction of II by lithium, perhaps via the reactive unstable dichlorobutadiyne<sup>15</sup>.

The isolation of the internal acetylene (III) using lithium or sodium, in contrast to the formation of the conjugated acetylene (IV) using magnesium, is not readily explained currently. A simple scheme for the production of bis(trimethylsilyl)-

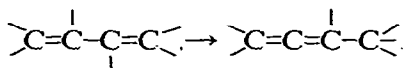
butadiyne (IV) is to assume initial dechlorination of hexachlorobutadiene to dichlorobutadiene.



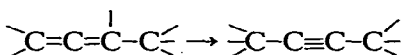
Reaction of more magnesium with this chlorocarbon might give the di-Grignard compound of butadiyne which would then couple with chlorotrimethylsilane to give IV<sup>16,17</sup>.

The formation of hexakis(trimethylsilyl)-2-butyne (III) from lithium (or sodium), chlorotrimethylsilane and II obviously involves an extensive rearrangement, although at which stage this occurs is not clear. Hexachloro-2-butyne has not been described although the fluorine analog is well known<sup>18</sup>. Trimethylsilyllithium has recently been described<sup>19</sup> and this may be formed transiently from chlorotrimethylsilane (or hexamethyldisilane) and lithium; this would presumably react with hexachloro-2-butyne to give III. Since it is not known at which stage rearrangement occurs, an alternative speculative scheme could be stepwise interaction of trimethylsilyllithium with hexachlorobutadiene. This scheme includes full trimethylsilylation of II giving the unknown hexakis(trimethylsilyl)-1,3-butadiene and subsequent rearrangement to III, although this is not considered a likely reaction pattern.

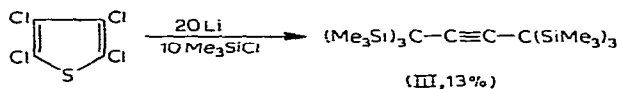
Accompanying the formation of III from lithium, chlorotrimethylsilane and hexachlorobutadiene are various amounts (0-5% using THF as solvent, and 11% using tetrahydro-2-methylfuran as solvent) of tetrakis(trimethylsilyl)allene (I). Compound I is formed in a side-reaction during the production of III; possible rearrangement to a 1,2-diene occurs as an alternative to rearrangement to a 2-alkyne. Rupture



of the terminal single bond might then produce compounds such as I. Rearrangement of a 1,2-diene to a 2-alkyne provides an alternative route to the production of III.



Interest in the reaction leading to III prompted a study of the reaction of tetrachlorothiophene, lithium (or magnesium) and chlorotrimethylsilane. Using lithium and the chlorosilane in THF afforded a 13% yield of III whereas magnesium and chlorotrimethylsilane gave no detectable amount of III although a large number



of products was obtained. The fate of the sulphur atom is uncertain although we have detected hydrogen sulfide on hydrolysis of the reaction product; this may be produced from lithium sulfide or hexamethyldisilthian since the Si-S bond is readily broken by water<sup>20</sup>. The reaction could proceed by initial attack of lithium on the heteroatom producing lithium sulfide and a dianion radical which upon trimethylsilylation and rearrangement could eventually give III. Another scheme would provide for trimethylsilylation of the tetrachlorothiophene with ring rupture in the later stages of

the reaction. We have not isolated any 2,3,4,5-tetrakis(trimethylsilyl)thiophene in these reactions. Hexakis(trimethylsilyl)benzene has not been described, although the less sterically hindered hexakis(dimethylsilyl)benzene has been synthesized from hexabromobenzene, magnesium and chlorodimethylsilane<sup>7</sup>.

Hexakis(trimethylsilyl)-2-butyne (III) exhibits considerable unreactivity towards normal chemical reagents known to attack the acetylenic bond. This is very probably due in large part to the steric hindrance of the six trimethylsilyl groups. Such a conclusion is supported by the relative inertness of the similarly sterically hindered bis(tert-butyl)acetylene which is not reduced by sodium in liquid ammonia<sup>21</sup>, nor does it react on refluxing with triphenylaluminum for many hours<sup>22</sup>. We have tried to synthesize *cis*-1,1,1,4,4,4-hexakis(trimethylsilyl)-2-butene (V) by catalytic

TABLE 2

SUMMARY OF SOME CHEMICAL REACTIONS ATTEMPTED WITH HEXAKIS(TRIMETHYLSILYL)-2-BUTYNE(III)

Reactant	Conditions of reactions	Products
<i>(a) Addition to triple bond</i>		
Cl <sub>2</sub>	CCl <sub>4</sub> solution, 20°, large excess of Cl <sub>2</sub>	HCl, unidentified polymeric material
Br <sub>2</sub>	CCl <sub>4</sub> solution, 20° Br <sub>2</sub> : III = 1 : 1	Me <sub>3</sub> SiBr, 66% unreacted III
HCl	C <sub>6</sub> H <sub>6</sub> solution, 20° large excess of HCl	No reaction
C <sub>6</sub> F <sub>5</sub> SiMe <sub>2</sub> H	C <sub>6</sub> H <sub>6</sub> solution, 80° H <sub>2</sub> PtCl <sub>6</sub> catalyst, 2 days	No reaction
C <sub>6</sub> H <sub>5</sub> Li	Ether, 0°, 7 h	No reaction
Li(CuMe <sub>2</sub> )	Ether, -10°, 12 h	No reaction
=CCl <sub>2</sub> (from Me <sub>3</sub> COK, CHCl <sub>3</sub> )	Hexane, 0°, 4 h	No reaction
<i>(b) Hydrogenolysis</i>		
H <sub>2</sub>	Cyclohexane, 200°/50 atm. Pd-charcoal catalyst, 5 h.	No reaction
H <sub>2</sub>	Hexane-ethyl acetate (2 : 1), 20°/1 atm., Pd-CaCO <sub>3</sub> catalyst, 2 days	No reaction
Na-liquid NH <sub>3</sub>	THF co-solvent	No reaction
<i>(c) Oxidation</i>		
SeO <sub>2</sub>	Decalin, 189°, 4 h	No reaction
KMnO <sub>4</sub>	Acetone, 56°, 2 h	Little or no reaction
CrO <sub>3</sub>	Acetic acid, 118°, 7 h	No isolable products, 30% recovered III
<i>(d) Hydrolysis or cleavage</i>		
NaOH	Homogenous and heterogenous systems	No definite product, much recovered III
H <sub>2</sub> SO <sub>4</sub>	100°, 2 h	Indefinite products, some recovered III
Me <sub>3</sub> COK, Me <sub>2</sub> SO	Ether	No definite products
Li, Me <sub>3</sub> SiCl	THF and 2-MeTHF, 18 h	No reaction
<i>(e) Diels-Alder</i>		
Hexachlorocyclopentadiene	Xylene, 138°, 4 days	No reaction

hydrogenation of (III) at 200°/50 atmospheres using a palladium–charcoal catalyst in cyclohexane but only unreacted III was recovered. An attempted reduction of III by sodium in liquid ammonia, which would presumably lead to the *trans*-isomer of V failed, although this compound is less sterically hindered than the *cis*-isomer.

Attempts to effect addition to the triple bond using a variety of reagents and conditions have also failed; however, we have observed a reaction with bromine which gives bromotrimethylsilane as one product. Chlorine also reacts with III to give an indefinite probably polymeric material and hydrogen chloride. Presumably in both cases cleavage occurs of the silicon–carbon bond.

In another approach, oxidation using both mild and vigorous oxidizing agents gave only a slow reaction, producing unidentified materials and much recovered III. An attempted Diels–Alder reaction with hexachlorocyclopentadiene and III gave no perceptible reaction in boiling xylene after 4 days.

The several attempted or uncertain reactions are summarized in Table 2.

As would be expected from a highly symmetrical structure, III is easily sublimable. In a sealed tube it is stable to 420°.

#### EXPERIMENTAL

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. Melting points are uncorrected. 1,2-Dimethoxyethane, diethyl ether, THF, tetrahydro-2-methylfuran, tetrahydro-2,2,4,4-tetramethylfuran and tetrahydropyran were dried over sodium and freshly distilled from sodium benzophenone ketyl before use. 1,4-Dioxane was refluxed over sodium and distilled before use. All other solvents were prepared anhydrous by standard procedures.

#### *Interaction of lithium, chlorotrimethylsilane and hexachloro-1,3-butadiene in THF*

Lithium (20.82 g, 3 g-atoms) was added, in small pieces, during 2 h to a vigorously stirred mixture of chlorotrimethylsilane (162.90 g, 1.5 moles) and hexachlorobutadiene (39.12 g, 0.15 mole) in 460 ml of THF. An exothermic reaction occurred with darkening of the solution and the precipitation of lithium chloride. After stirring for a total of 20 h, excess lithium was removed by filtration and the product hydrolyzed with 2*N* hydrochloric acid. The organic products were extracted with ether, the ethereal layer dried over anhydrous magnesium sulfate, concentrated and the volatiles removed at 18 mm. A dark solid remained which was washed well with absolute ethanol, giving white crystals. Recrystallization from hexane afforded 29.35 g (40%) of hexakis(trimethylsilyl)-2-butyne (III), *m.p.* 276–277°, as white plates. (Found: C, 54.6; H, 11.05; Si, 34.0, 34.1; mol. wt., 487 (mass spectrometry).  $C_{22}H_{54}Si_6$  calcd.: C, 54.25; H, 11.2; Si, 34.6%; mol. wt., 487.) An NMR spectrum of the product (in carbon tetrachloride) showed a singlet at  $\tau$  9.80 (Si–Me protons). The Raman spectrum of III showed a line at  $2144\text{ cm}^{-1}$  ( $C\equiv C$ ).

Concentration of the alcohol washings of III gave a dark oil which was fractionally distilled to give tetrakis(trimethylsilyl)allene (I) (2.37 g, 4.8%) *b.p.* 65–66°/0.15 mm,  $n_D^{20}$  1.4765; (lit.<sup>5</sup> for (I): *b.p.* 68–70°/0.2 mm,  $n_D^{20}$  1.4770). The infrared spectrum was identical with an authentic specimen of I.

Virtually identical yields of III were obtained by the addition of hexachlorobutadiene to lithium and chlorotrimethylsilane in THF.

*Interaction of sodium, chlorotrimethylsilane and hexachlorobutadiene in THF*

Hexachlorobutadiene (6.52 g, 0.025 mole) dissolved in THF (40 ml) was added dropwise (2 h) to a vigorously stirred mixture of chlorotrimethylsilane (27.15 g, 0.25 mole) and sodium (11.5 g, 0.5 g-atom) in THF (150 ml). After initiation with a crystal of iodine an exothermic reaction occurred with darkening and the precipitation of a solid. Stirring was continued for 11 h and then work-up as described previously afforded a dark solid. After washing with absolute ethanol and recrystallization from hexane, 3.04 g (25%) of hexakis(trimethylsilyl)-2-butyne was obtained, m.p. and mixed m.p. with an authentic specimen, 276–277°.

Concentration of the alcohol washings gave, by VPC, a number of components. Infrared spectroscopy revealed the presence of acetylenic, allenic and olefinic bonds in these compounds.

*Interaction of magnesium, chlorotrimethylsilane and hexachlorobutadiene in THF*

Hexachlorobutadiene (26.08 g, 0.1 mole) dissolved in THF (50 ml) was added dropwise (3 h) to magnesium (48.64 g, 2 g-atoms) and chlorotrimethylsilane (108.6 g, 1 mole) in THF (150 ml). An exothermic reaction occurred and magnesium chloride was precipitated from a dark solution. After 8 h of vigorous stirring, work-up as before gave a dark solid and a viscous oil. Examination of these products by VPC revealed the presence of one major component and at least 21 minor components. The products were dissolved in hexane and chromatographed from neutral alumina, with hexane as the eluent. Bis(trimethylsilyl)-1,3-butadiyne (IV), (8.6 g, 44%) was obtained as a very pale yellow solid; m.p. and mixed m.p. with an authentic sample<sup>2,3</sup> 106–107°. (Found: Si, 28.7. C<sub>10</sub>H<sub>18</sub>Si<sub>2</sub> calcd.: Si, 28.9%.)

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