

## NOTE

POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL  
COMPOUNDSXX\*. SOME ORGANOSILICON DERIVATIVES PREPARED VIA  
METALATION OF 1,3,5-TRICHLOROBENZENE

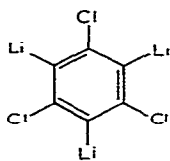
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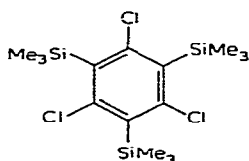
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The metalation of highly halogenated benzenes can be achieved by either halogen-metal or hydrogen-metal exchange. Thus, hexachlorobenzene, treated with *n*-butyllithium undergoes a halogen-metal exchange, to yield pentachlorophenyl-lithium<sup>2</sup>, but pentachlorobenzene<sup>3</sup>, 1,2,4,5-tetrachlorobenzene<sup>3</sup> and 1,2,3,4-tetrachlorobenzene<sup>4</sup> undergo hydrogen-metal exchange, with the formation of the corresponding mono- and dilithio-polychlorobenzenes. It was, therefore, interesting to establish, in connection with some cyclic compounds, if the symmetrical 1,3,5-trichlorobenzene will replace the halogen or the hydrogen with lithium, when treated with *n*-butyllithium.

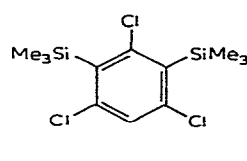
We found that the treatment of 1,3,5-trichlorobenzene with *n*-butyllithium (molar ratio 1 : 3) in tetrahydrofuran (THF) at  $-65^{\circ}$ , results in a hydrogen metal interchange, with the formation of 1,3,5-trichloro-2,4,6-trilithiobenzene (I). The organolithium compound thus formed was used, without isolation, for the preparation of 1,3,5-trichloro-2,4,6-tris(trimethylsilyl)benzene (II) by derivatisation with trimethylchlorosilane. The isolation of 1,3,5-trichloro-2,6-bis(trimethylsilyl)benzene (III) from the same reaction product showed that the metalation under our conditions was not complete.



(I)



(II)



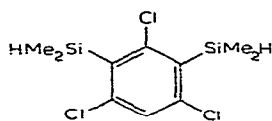
(III)

\* For Part XIX see ref. 1.

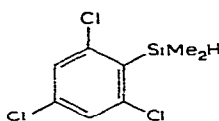
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When the molar ratio  $n\text{-BuLi}/1,3,5\text{-Cl}_3\text{C}_6\text{H}_3$  was 3 : 1, the yield of pure (II) was 37.7%. Although it appears that more of this product can be recovered from the reaction mixture, no attempt to improve the yield was made at this stage. With a molar ratio  $n\text{-BuLi}/1,3,5\text{-Cl}_3\text{C}_6\text{H}_3$  of 2 : 1, only a trace of (II) was identified by vapor phase chromatography, and the yield of (III) was 43.8%. According to VPC in both cases, the reaction mixtures contained a more volatile compound, in small proportion, believed to be 1,3,5-trichloro-2-(trimethylsilyl)benzene, but this compound has not been isolated pure.

In a similar way, two dimethylsilyl derivatives, (IV) and (V), were prepared by derivatising the organolithium reagent made from 1,3,5-trichlorobenzene, with dimethylchlorosilane.



(IV)



(V)

The compounds were identified by means of elemental analysis, and molecular weight determination (mass spectrometry). Proton magnetic resonance was used in addition to confirm the structure of these compounds. The spectra of compounds (III) and (V) are presented as illustrations. Thus, compound (III) contains peaks due to aromatic proton resonance ( $\tau$  2.53) and  $\text{SiCH}_3$  proton resonance ( $\tau$  9.22) in 1 : 18 integrated area ratio [expected for structure (III), 1 : 18]. The PMR spectrum of (V) contains a peak due to aromatic protons ( $\tau$  2.74), a multiplet (five lines) due to  $\text{SiH}$  protons (centered at  $\tau$  4.95) and a doublet due to  $\text{SiCH}_3$  protons (with  $\tau$  9.40 and 9.46), in the ratio of integrated areas 2 : 1 : 6 [expected for structure (V), 2 : 1 : 6].

#### EXPERIMENTAL

##### 1,3,5-Trichloro-2,4,6-tris(trimethylsilyl)benzene (II)

A solution of 18.14 g (0.1 mole) of 1,3,5-trichlorobenzene in 250 ml THF (dried over sodium metal and distilled over sodium benzophenone ketyl before use) was treated with 192 ml of a solution of *n*-butyllithium in *n*-hexane, containing 19.2 g *n*-BuLi (0.3 mole), at  $-65^\circ$ , and stirred at low temperature until Color Test II<sup>5</sup> was negative (showing the complete consumption of *n*-BuLi). Color Test I<sup>6</sup> was positive, indicating the presence of an organometallic reagent. The reaction mixture was then treated with 32.5 g of trimethylchlorosilane (0.3 mole) dissolved in 50 ml THF. The reaction mixture was stirred for an additional 30 min at  $-65^\circ$ , then allowed to reach room temperature overnight. The precipitate deposited was found to consist of lithium chloride and was filtered. The filtrate was concentrated on a rotary evaporator to give a mixture of an oil and crystals (37.7 g). The crystals were separated, recrystallized from petroleum ether (b.p.  $60\text{--}70^\circ$ ) and vacuum dried, to give 15.0 g 1,3,5-trichloro-2,4,6-tris(trimethylsilyl)benzene (II), m.p.  $147^\circ$  (pure yield 37.7%). (Found: C, 45.47, 45.34; H, 6.74, 6.9; mol. wt. mass spec., 397.  $\text{C}_{15}\text{H}_{27}\text{Cl}_3\text{Si}_3$  calcd.: C, 45.26; H, 6.80%; mol. wt., 397.6.) Ultraviolet spectrum,  $\lambda_{\text{max}}$  ( $\epsilon \cdot 10^3$ ); 229  $m\mu$  (27); 246  $m\mu$  (8.5); 285  $m\mu$  (0.4) and 293  $m\mu$  (0.4).

*1,3,5-Trichloro-2,6-bis(trimethylsilyl)benzene (III)*

A solution of 9.1 g (0.05 mole) of 1,3,5-trichlorobenzene in 150 ml THF, cooled at  $-65^{\circ}$ , was treated with 64 ml solution of n-butyllithium in n-hexane, containing 6.4 g (0.1 mole) of n-BuLi, and stirred 0.5 h at low temperature. After Color Test II was negative, the mixture was treated with 10.8 g (0.1 mole) trimethylchlorosilane dissolved in 50 ml THF and, after 1 h of stirring, was concentrated in a rotary evaporator, diluted with petroleum ether (b.p.  $60-70^{\circ}$ ) and evaporated again, to give 14.7 g of an oil. The oil was distilled on a spinning band column, and a fraction boiling at  $82-84^{\circ}/0.05$  mm was found pure by VPC. Yield 7.1 g (43.8%). It consisted of 1,3,5-trichloro-2,6-bis(trimethylsilyl)benzene (III). (Found: C, 43.96, 44.19; H, 5.86, 5.92; mol.wt. mass spec., 325.  $C_{12}H_{19}Cl_3Si_2$  calcd.: C, 44.21; H, 5.84%; mol.wt., 325.) Ultraviolet spectrum:  $\lambda_{max} (\epsilon \cdot 10^3)$ : 214  $m\mu$  (21.9); 223  $m\mu$  (34.4); 238  $m\mu$  (7.7); 288  $m\mu$  (0.4); 296  $m\mu$  (0.3).

*1,3,5-Trichloro-2,6-bis(dimethylsilyl)benzene (IV) and 1,3,5-trichloro-2-(dimethylsilyl)benzene (V)*

These compounds were prepared as described above for (III), from 18.14 g 1,3,5-trichlorobenzene, 128 ml solution of n-butyllithium in n-hexane, 15%, and 18.8 g  $Me_2HSiCl$ . After a similar treatment, the reaction mixture was distilled on a spinning band column. The fraction boiling at  $71-72^{\circ}/0.07$  mm was found to consist of 1,3,5-trichloro-2-(dimethylsilyl)benzene (V), yield, 15.3 g. (Found: C, 40.87, 40.92; H, 3.73, 3.92; mol.wt. mass spec., 239.  $C_8H_9Cl_3Si$  calcd.: C, 40.10; H, 3.75%; mol.wt., 239.4.) Another fraction (5.5 g) boiling at  $86-88^{\circ}/0.1$  mm, solidified on standing, to give crystals with m.p.  $46-48^{\circ}$ . After recrystallization from n-pentane, pure 1,3,5-trichloro-2,6-bis(dimethylsilyl)benzene (IV), m.p.  $53-54^{\circ}$  was obtained. (Found: C, 40.67, 40.63; H, 4.95, 4.96; mol.wt. mass spec., 297.  $C_{10}H_{15}Cl_3Si_2$  calcd.: C, 40.33; H, 5.04%; mol.wt., 297.5.)

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