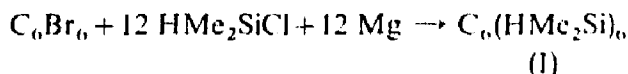


NOTE

Polyhalo-organometallic and -organometalloidal compounds XV*. Some reactions of hexabromobenzene

Incidental to studies concerned with thermally stable polymers, it was desirable to compare analogous polyfluoro-, polychloro- and polybromo-types. One of the reactive functional groups useful for the preparation of polymers is $\text{HMe}_2\text{Si}-$. Compounds such as *p*- $\text{HMe}_2\text{SiC}_6\text{Cl}_4\text{SiMe}_2\text{H}$ and *p*- $\text{HMe}_2\text{SiC}_6\text{F}_4\text{SiMe}_2\text{H}$ have been prepared¹. In addition to examining the preparation of the corresponding tetrabromo compound, it appeared of interest to prepare monomers having a plurality of $\text{HMe}_2\text{Si}-$ groups. One approach is by the use of $(\text{HMe}_2\text{Si})_3\text{SiLi}$ which is conveniently available².

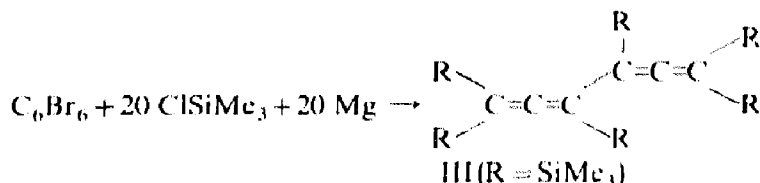
Incidental to studies on compounds having more than one $\text{HMe}_2\text{Si}-$ group and more than one nuclear halogen, we have observed that the following reaction occurs between hexabromobenzene, chlorodimethylsilane and magnesium in tetrahydrofuran (THF):



This hexakis(dimethylsilyl)benzene is being examined as a reactive polyfunctional monomer in polymer formation and also in relation to studies concerned with polytrimethylsilylated-benzenes and with the so-called "allene" reaction³.

Hexabromobenzene, by analogy with hexachlorobenzene³, gave rise to tetrakis(trimethylsilyl)allene (II) in a prompt reaction with excess lithium and chlorotrimethylsilane in THF. This is in contrast to hexafluorobenzene which does not react to give the allene (II) under corresponding conditions³.

Although a molecular model of hexakis(dimethylsilyl)benzene had predicted it to be sterically possible, a similar model of hexakis(trimethylsilyl)benzene could not be made. Correspondingly, no poly(trimethylsilylated)benzene derivative could be isolated from an *in situ* reaction of hexabromobenzene with excess magnesium and chlorotrimethylsilane; all that we have so far isolated from such a reaction was a small amount of what appears to be 1,1,3,4,6,6-hexakis(trimethylsilyl)-1,2,4,5-hexatetraene (III):



Details of these latter reactions will be reported later.

* For part XIV see ref. 1.

Experimental

Reactions were carried out under an atmosphere of dry oxygen-free nitrogen. THF was dried over sodium and distilled from sodium benzophenone ketyl before use.

Hexakis(dimethylsilyl)benzene (I). Hexabromobenzene (22.08 g, 0.04 mole) in THF (150 ml) was added to a mixture of chlorodimethylsilane (45.3 g, 0.48 mole) and magnesium (12.15 g, 0.48 g-atom) in THF (50 ml) with stirring. Reaction occurred immediately. On completion of the addition, the reaction mixture was heated at reflux for 12 h. The mixture was hydrolyzed in dilute acid and the hydrolysate extracted with ether. Removal of volatile solvents left a solid and some oil. The solid was isolated and sublimed at 150°/0.1 mm to afford hexakis(dimethylsilyl)benzene (I), (4.6 g, 27%), m.p. 204–206°. The compound was very soluble in the common organic solvents. The IR spectrum of (I) showed characteristic bands (cm^{-1}) for C–H (2900, 2970), Si–H (2150) and Si–Me (1242). The ^1H NMR spectrum of (I) showed Si–Me (doublet; 9.5, 9.55 τ) and Si–H (multiplet, 5.06–5.38 τ) protons in the integrated ratio 6.2:1. [calcd. ratio for (I) 6:1]. [Found: C, 51.1; H, 9.88; Si, 39.3; mol. wt. (mass spectrum), 426. $\text{C}_{18}\text{H}_{42}\text{Si}_6$ calcd.: C, 50.71; H, 9.8; Si, 39.44%; mol. wt., 426.]

A previous run of this reaction under analogous conditions and using the same quantities of reactants gave hexakis(dimethylsilyl)benzene in 14.7% yield.

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- 1 K. SHIINA, T. BRENNAN AND H. GILMAN, *J. Organometal. Chem.*, 11 (1968) 471.
- 2 H. GILMAN, J. M. HOLMES AND C. L. SMITH, *Chem. Ind. (London)*, (1965) 848.
- 3 K. SHIINA AND H. GILMAN, *J. Amer. Chem. Soc.*, 88 (1966) 5367; F. W. G. FEARON AND H. GILMAN, *Chem. Commun.*, (1967) 86.

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