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POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS

XXII*. THE REACTION OF TRIPHENYLSILYLLITHIUM WITH HEXAFLUOROBENZENE

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SUMMARY

The reaction of triphenylsilyllithium with an *excess* of hexafluorobenzene at low temperatures gave hexaphenyldisilane [compound (II)] and 1,4-bis(triphenylsilyl)tetrafluorobenzene [compound (III)] instead of the expected (pentafluorophenyl)triphenylsilane [compound (I)]. In an attempt to account for the formation of these products, the reactions of triphenylsilyllithium with certain organosilicon-substituted polyfluorobenzenes were investigated and are described.

In contrast to the above reactions, triphenylsilyllithium reacted with hexachlorobenzene via halogen–metal exchange to give pentachlorophenyllithium and hexaphenyldisilane.

INTRODUCTION

As part of a general investigation into the preparation and comparison of the properties of perhalophenyl-substituted organosilicon compounds, we wished to obtain (pentafluorophenyl)triphenylsilane, (I). A possible route to this compound appeared to be via the reaction of triphenylsilyllithium with hexafluorobenzene.

Hexafluorobenzene has been shown to react with approximately equivalent amounts of alkyl[1,2] or aryllithium[3] compounds to give good yields of alkyl- or aryl-substituted pentafluorobenzenes. However, appreciable amounts of disubstituted products were frequently isolated from these reactions. In view of this fact, it appeared that to favor the formation of compound (I), triphenylsilyllithium should be added to a large excess of hexafluorobenzene at low temperature.

RESULTS AND DISCUSSION

Triphenylsilyllithium (x moles) reacted rapidly when added to a solution of hexafluorobenzene (4x moles) in THF at −70°, but no compound (I)[4] could be detected in the reaction mixture. The major products isolated were hexaphenyldisilane, (II), (20.6%) and a solid m.p. 291–292° which appeared from elemental ana-

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lysis, molecular weight and spectral examinations to be 1,4-bis(triphenylsilyl)tetrafluorobenzene, (III), (38.3 %). In addition, an appreciable quantity of a white solid was obtained which was insoluble in all common organic solvents and which did not melt below 430°. The infrared spectrum of this material (KBr) indicated the presence of $-SiPh$ and $-C_6F_n$ moieties.

The identity of compound (III) was confirmed by an independent synthesis from 1,4-dilithiotetrafluorobenzene[5] and bromotriphenylsilane.

Two main points of interest were raised by the reaction of triphenylsilyllithium with hexafluorobenzene:

(*a*) No compound (I) could be detected in a reaction which should have favoured its formation.

(*b*) Compound (II) had frequently been obtained as a product from reactions of triphenylsilyllithium with various halogen-containing compounds[6]. In all cases, the formation of compound (II) was explained in terms of the following halogen–metal exchange:

$$Ph_3SiLi + RX \rightarrow Ph_3SiX + RLi$$

$$Ph_3SiLi + Ph_3SiX \rightarrow \underset{\text{(II)}}{Ph_6Si_2} + LiX$$

There appeared to be no reported examples of an exchange reaction of this type occurring between hexafluorobenzene and a metallic reagent.

It is reasonable to suppose that compound (III) was formed via a two stage reaction of triphenylsilyllithium with hexafluorobenzene:

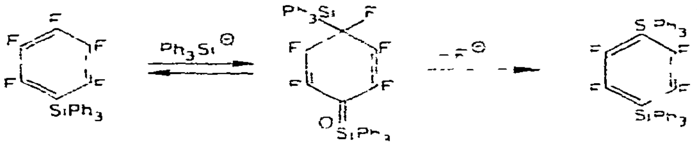
$$Ph_3SiLi + C_6F_6 \rightarrow Ph_3SiC_6F_5 + LiF \qquad (1)$$

$$Ph_3SiLi + Ph_3SiC_6F_5 \rightarrow \underset{\text{(III)}}{Ph_3SiC_6F_4SiPh_3} + LiF \qquad (2)$$

The reaction was carried out using a considerable excess of hexafluorobenzene; thus, as no compound (I) could be detected, reaction (2) was apparently considerably faster than reaction (1). This suggests that the introduction of one triphenylsilyl-group into the hexafluorobenzene nucleus strongly activated the *p*-fluorine atom to nucleophilic attack, so that a further molecule of triphenylsilyllithium reacted at this position, rather than with the excess of hexafluorobenzene.

Triphenylsilyllithium reacted virtually instantaneously with compound (I) at −70° to give an 83 % yield of compound (III). No compound (II), or high melting material was isolated from this reaction.

The explanation of the powerful activating effect of the triphenylsilyl-group on the *p*-fluorine atom may be similar to that put forward to account for the high reactivity of certain pentafluorophenyl-substituted thioethers towards the ethoxide and thiophenoxide ions[7]. It was postulated that substitution of the *p*-fluorine atom by either of the aforementioned ions proceeded via an addition–elimination mechanism, the intermediate ionic addition compound being stabilised by the use of the vacant *d*-orbitals of the sulfur atom. There is a large amount of evidence to suggest that silicon can make similar use of its *d*-orbitals[8]. It is thus conceivable that the rapid reaction of triphenylsilyllithium with compound (I) might have proceeded via a



(I) (III)

similar addition–elimination mechanism.

It is known that the trimethylsilyl-group does not withdraw electrons as powerfullly as the triphenylsilyl-group[8]. It was thus of interest to examine the reaction of triphenylsilyllithium with (pentafluorophenyl)trimethylsilane, (IV).

Triphenylsilyllithium (x moles) was added to compound (IV) (x moles) at $-70°$. After *ca.* 45 min, no triphenylsilane could be detected by GLC in an acid-hydrolysed sample of the reaction mixture, indicating that all of the triphenylsilyllithium had been consumed. However, the raction mixture still gave a positive Color Test I, indicating that an active metallic species remained. Carbonation with gaseous carbon dioxide at $-70°$ rapidly consumed this metallic species: 42.5% of the expected 1-(trimethylsilyl)-4-(triphenylsilyl)tetrafluorobenzene, (V), was isolated together with 5.3% of pentafluorobenzoic acid and 2.0% of 1,1,1-trimethyl-2,2,2-triphenyldisilane, (VI). The identity of compound (V) was confirmed by the following syntheses from 1,2,4,5-tetrafluorobenzene:

$$\text{H–C}_6\text{F}_4\text{–H} + \text{n-BuLi} \xrightarrow[-70°]{\text{THF}} \text{H–C}_6\text{F}_4\text{–Li} \xrightarrow{\text{Me}_3\text{SiCl}} \text{H–C}_6\text{F}_4\text{–SiMe}_3$$

$$\text{H–C}_6\text{F}_4\text{–SiMe}_3 + \text{n-BuLi} \xrightarrow[-70°]{\text{THF}} \text{Li–C}_6\text{F}_4\text{–SiMe}_3 \xrightarrow{\text{Ph}_3\text{SiBr}} \underset{\text{(V)}}{\text{Ph}_3\text{Si–C}_6\text{F}_4\text{–SiMe}_3}$$

The isolation of pentafluorobenzoic acid and compound (VI) from the reaction of triphenylsilyllithium with compound (IV) indicated that the following cleavage reaction had occurred to a limited extent.

$$\text{C}_6\text{F}_5\text{SiMe}_3 + \text{Ph}_3\text{SiLi} \rightarrow \text{C}_6\text{F}_5\text{Li} + \text{Ph}_3\text{SiSiMe}_3$$

A similar type of cleavage reaction had previously been shown to occur when (pentafluorophenyl)diphenylsilane was treated with an organolithium reagent[4]:

$$\begin{array}{l} \text{C}_6\text{F}_5\text{Ph}_2\text{SiH} + \text{RLi} \rightarrow \text{C}_6\text{F}_5\text{Li} + \text{RPh}_2\text{SiH} \\ \qquad\qquad\qquad\qquad\quad \Big\downarrow \text{Me}_3\text{SiCl} \\ \qquad\qquad\qquad\qquad\quad \text{C}_6\text{F}_5\text{SiMe}_3 \qquad (\text{R}=\text{Me or n-Bu}) \end{array}$$

The above cleavage reactions suggested that a possible source of the compound (II) isolated from the reaction of triphenylsilyllithium with hexafluorobenzene might have been the attack of triphenylsilyllithium on compound (III) formed during the reaction:

$$\text{Ph}_3\text{SiC}_6\text{F}_4\text{SiPh}_3 + \text{Ph}_3\text{SiLi} \rightarrow \text{Ph}_3\text{SiSiPh}_3 + \underset{\text{(VII)}}{[\text{Ph}_3\text{SiC}_6\text{F}_4\text{Li}]}$$

This idea received some support from the observation that reaction of triphenylsilyllithium with hexafluorobenzene using a 2:1 molar ratio gave less of compound (III) (9.1%) and more of compound (II) (37%), than the 1:4 molar ratio reaction.

Compound (III) (x moles) reacted slowly with triphenylsilyllithium (2x moles) at −70°. After 2 h excess chlorotrimethylsilane was added. Unreacted compound (III) (54%) was isolated together with 12.4% of compound (II). No compound (V) could be detected; this should have readily been formed had there been a significant quantity of compound (VII) present. There was no evidence for the formation of any poly(triphenylsilyl)polyfluorobenzenes, which might have been expected from further nucleophilic attack of triphenylsilyllithium on compound (III). This last point was of considerable significance for, until this stage, it was possible that the high-melting material mentioned previously, might have been composed of such compounds. The only other product that was isolated from this reaction was 37% of compound (VI), presumably formed by the reaction of chlorotrimethylsilane with unreacted triphenylsilyllithium.

The fact that triphenylsilyllithium reacted only slowly with compound (III) to give some compound (II), suggests that this reaction was probably not the major source of compound (II) in the rapid reactions of triphenylsilyllithium with hexafluorobenzene.

Another possible source of compound (II) was via the aforementioned halogen–metal exchange reaction:

$$C_6F_6 + Ph_3SiLi \rightarrow Ph_3SiF + C_6F_5Li$$
$$Ph_3SiF + Ph_3SiLi \rightarrow Ph_3SiSiPh_3 + LiF$$

However, no pentafluorophenyllithium could be detected when triphenylsilyllithium (x moles) was added to hexafluorobenzene (4x moles) at −70°, followed by addition of chlorotrimethylsilane. If any of the lithium compound had been present, some compound (IV) should have been formed.

It had been shown[9] that triphenylsilylsodium gave less of compound (II) than did triphenylsilyllithium when reacted with a series of organic halides, presumably because less halogen–metal exchange had occurred. Treatment of hexafluorobenzene (4x moles) with triphenylsilylsodium (x moles) at −70° gave similar amounts of compound (II) (19.7%) and compound (III) (33.4%) to those obtained from the corresponding reaction with triphenylsilyllithium.

From the above reactions, it is apparent that at the present time, there is no satisfactory explanation for the formation of compound (II) during the reactions of triphenylsilylmetallic compounds with hexafluorobenzene.

The high-melting material that was isolated from all of the reactions of hexafluorobenzene with triphenylsilylmetallic compounds has not been characterised. However, the physical properties of this material, together with its infrared spectrum, suggest that it may be polymeric in nature.

The reaction of triphenylsilyllithium (x moles) with hexachlorobenzene (x moles) was carried out at −70°, followed by treatment with chlorotrimethylsilane. The isolation of compound (II) (79%) and (pentachlorophenyl)trimethylsilane (46%), suggested that the following halogen–metal exchange had occurred to a large extent:

$$\begin{tikzcd} C_6Cl_6 + Ph_3SiLi \arrow[r, "THF", "-70^\circ"'] & Ph_3SiCl + C_6Cl_5Li \arrow[r, "Me_3SiCl"] \arrow[d, "Ph_3SiLi"] & C_6Cl_5SiMe_3 \\ & Ph_3SiSiPh_3 & \end{tikzcd}$$

(II)

It is significant that no triphenylsilyl-substituted polychlorobenzenes were isolated from this reaction.

EXPERIMENTAL

Reactions were carried out under dry oxygen-free nitrogen. THF was purified by distillation from sodium–benzophenone ketyl. Triphenylsilyllithium[6] and triphenylsilylsodium[9] were prepared from compound (II) by the reported procedures; these solutions were carefully filtered to remove any traces of unreacted compound (II) before use. Bromotriphenylsilane[10] and compound (I)[4] were prepared by the reported procedures. n-Butyllithium in hexane was obtained from the Foote Mineral Co. Molecular weights were determined by mass spectroscopy. GLC analyses were carried out with an F and M Model 500 Gas Chromatograph using an $18 \times \frac{1}{4}''$ column packed with silicon gum rubber, SE 30, on Chromosorb W (1:20). All melting points are uncorrected. Unless otherwise stated, all products were identified by comparison with authentic materials.

Reactions of triphenylsilylmetallic compounds with hexafluorobenzene

(*a*) *Triphenylsilyllithium* (0.05 *mole*) *and hexafluorobenzene* (0.2 *mole*). A solution of triphenylsilyllithium (0.05 mole) in THF (75 ml) was added dropwise with rapid stirring to a solution of hexafluorobenzene (37.2 g, 0.2 mole) in THF (100 ml) at −70° during 30 min. The dark-brown color of the silyllithium compound was rapidly discharged and the solution turned light purple. After the addition, Color Test I[11] was negative. The mixture, containing much precipitated solid, was allowed to warm to room temperature before being concentrated. The residue was extracted with hot toluene (2 × 400 ml) and filtered. The residue, after prolonged extraction with water, left a solid (5.7 g) which did not melt below 430°. The combined toluene filtrates on cooling deposited compound (II) and more of this compound was obtained by concentration of the mother liquors. The total amount of compound (II) isolated was 2.7 g (20.6%). The residual toluene mother liquors were concentrated and the residue was treated with petroleum ether (b.p. 60–80°) and filtered. No compound (I) could be detected in the petroleum ether filtrate by GLC. The residue left after extraction with petroleum ether was recrystallised from a benzene/toluene mixture (*ca.* 50%) to give 1,4-bis(triphenylsilyl)tetrafluorobenzene, m.p. 291–292° (6.4 g, 38.3%). (Found: C, 75.5; H, 4.61; mol.wt., 666. $C_{42}H_{30}F_4Si_2$ calcd.: C, 75.67; H, 4.51%; mol.wt., 666.4.)

(*b*) *Triphenylsilyllithium* (0.05 *mole*) *and hexafluorobenzene* (0.2 *mole*) *followed by treatment with chlorotrimethylsilane.* Reaction (*a*) was repeated under identical conditions. When all of the triphenylsilyllithium had reacted, excess chlorotrimethylsilane was added. The reaction was worked up as described above to give 36% of compound (III) and 23.2% of compound (II). No (pentafluorophenyl)trimethylsilane could be detected in the reaction mixture by GLC.

(*c*) *Triphenylsilyllithium* (0.05 *mole*) *and hexafluorobenzene* (0.025 *mole*). Triphenylsilyllithium (0.05 mole) in THF (75 ml) was added dropwise with stirring to hexafluorobenzene (4.65 g, 0.025 mole) in THF (50 ml) at −70°. The reaction mixture turned blue and Color Test I was negative on completion of the addition. The mixture was worked up essentially as described above, except that it was necessary to extract the initial residue with 4 × 400 ml of hot toluene to remove all of compound (II). This reaction yielded 37% of compound (II) and 9.1% of compound (III).

(*d*) *Triphenylsilylsodium* (0.05 *mole*) *and hexafluorobenzene* (0.2 *mole*). Triphenylsilylsodium (0.05 mole) in THF (75 ml) was added to hexafluorobenzene (37.2 g, 0.2 mole) in THF (100 ml) at −70°. An immediate reaction occurred, the solution turned purple and Color Test I was negative immediately after the addition. A similar workup to that previously described gave 19.7% of compound (II) and 33.4% of compound (III).

Reaction of (pentafluorophenyl)triphenylsilane (I) with triphenylsilyllithium

Triphenylsilyllithium (0.005 mole) in THF (10 ml) was added to compound (I) (2.1 g, 0.005 mole) in THF (20 ml) at −70°. An immediate reaction occurred and Color Test I was negative directly after the addition. The solution was warmed to room temperature, concentrated and the residue extracted with toluene (50 ml). The toluene extracts were concentrated and diluted with benzene to give compound (III) (2.8 g, 83%).

Reaction of (pentafluorophenyl)trimethylsilane with triphenylsilyllithium

Triphenylsilyllithium (0.05 mole) in THF (75 ml) was added to (pentafluorophenyl)trimethylsilane (12.0 g, 0.05 mole) in THF (75 ml) during 15 min. The reaction mixture turned dark-brown and Color Test I remained positive after the addition. However, no triphenylsilane and little (pentafluorophenyl)trimethylsilane could be detected in a hydrolysed aliquot by GLC. Gaseous carbon dioxide was passed through the reaction mixture for 30 min, after which the mixture was allowed to warm to room temperature. The mixture was concentrated and the residual sticky solid was extracted with petroleum ether; the residue from this extraction was covered with THF and acidified. The THF solution was separated, dried, concentrated and the residue was crystallised from hexane to give pentafluorobenzoic acid (0.57 g, 5.3%). The petroleum ether solution was concentrated and the residue was recrystallised from methanol to give 1-(trimethylsilyl)-4-(triphenylsilyl)tetrafluorobenzene, m.p. 125–126° (10.2 g, 42.5%). (Found: C, 67.51; H, 4.77; mol. wt., 480. $C_{27}H_{24}F_4Si_2$ calcd.: C, 67.48; H, 4.99%; mol. wt., 480.4.)

The methanol mother liquors were concentrated and the residue was distilled under reduced pressure to give 1,1,1-trimethyl-2,2,2-triphenyldisilane (0.34 g, 2.0%).

Reaction of compound (III) with triphenylsilyllithium

Triphenylsilyllithium (0.015 mole) in THF (50 ml) was added dropwise with stirring to a suspension of compound (III) (5.0 g, 0.0075 mole) in THF (25 ml) at −70°. The solution turned blue and then dark-brown. After 2 h, Color Test I was still strongly positive and much triphenylsilane was present in an acid-hydrolysed sample.

Chlorotrimethylsilane (0.1 mole) was added. The mixture was worked up essentially as described above to give compound (II) (0.95 g, 12.4%) and unreacted compound (III) (2.7 g, 54%). No high-melting material was isolated. The residue obtained on concentration of the petrol filtrate was distilled under reduced pressure to give 1,1,1-trimethyl-2,2,2-triphenyldisilane (1.85 g, 37%)

Reaction of triphenylsilyllithium with hexachlorobenzene

Triphenylsilyllithium (0.05 mole) in THF (75 ml) was added dropwise with stirring to a suspension of hexachlorobenzene (28.5 g, 0.1 mole) in THF (75 ml) at −70°. After 30 min. Color Test I was still positive but no triphenylsilane could be detected by GLC in an acid hydrolysed aliquot of the reaction mixture. Chlorotrimethylsilane (10.8 g, 0.1 mole) was added and the reaction mixture was allowed to warm to room temperature and filtered. The residue was sublimed (150°/0.1 mm) to remove unreacted hexachlorobenzene (16.7 g, 58.6%). The sublimation residue was crystallised from xylene to give compound (II) (10 2 g, 79%). The THF solution was concentrated and the residue was extracted with benzene (20 ml). The benzene extracts were chromatographed over alumina (Woelm neutral grade). Elution of the column with petroleum ether gave a white solid which, on crystallisation from ethanol, gave (pentachlorophenyl)trimethylsilane (3.7 g, 46.0%).

Preparation of 1,4-*bis(triphenylsilyl)tetrafluorobenzene [compound (III)]*

A solution of 1,4-dilithiotetrafluorobenzene[5] (0.0125 mole) was prepared by the slow addition of 1,2,4,5-tetrafluorobenzene (0.0125 mole) in THF (50 ml) to n-butyllithium (0.025 mole) in hexane at −70°. After stirring for 30 min. a solution of bromotriphenylsilane (7.8 g, 0.025 mole) in THF (50 ml) was added. The mixture was stirred 16 h at −70° before being allowed to warm to room temperature during 3 h. Compound (III) (4.2 g, 49%) was isolated from the residue as previously described.

Preparation of 1-*(triphenylsilyl)*-4-*(trimethylsilyl) tetrafluorobenzene [compound (IV)]*

n-Butyllithium (0.1 mole) in hexane was added dropwise to a solution of 1,2,4,5-tetrafluorobenzene (15.0 g, 0.1 mole) in ether (100 ml) at −70°. The solution was stirred 30 min when chlorotrimethylsilane (10.8 g, 0.1 mole) in ether (25 ml) was added. The mixture was warmed to room temperature and hydrolysed with dilute hydrochloric acid. The ethereal layer was separated, dried and concentrated and the residue was distilled under reduced pressure to give 1-(trimethylsilyl)-2,3,5,6-tetrafluorobenzene, b.p. 70–71°/20 mm, (13 0 g, 56%). (Found: C, 48.62; H, 4.96; mol. wt., 222. $C_9H_{10}F_4Si$ calcd.: C, 48.62; H, 4.53%; mol. wt., 222.3.)

A solution of 1-(trimethylsilyl)-2,3,5,6-tetrafluorobenzene (4.9 g, 0.022 mole) in THF (50 ml) was added to n-butyllithium (0 022 mole) in hexane at −70°. The solution was stirred for 30 min when a solution of bromotriphenylsilane (6.8 g, 0.022 mole) in THF (50 ml) was added. The reaction mixture was stirred for 12 h at −70° when it was allowed to warm to room temperature during 3 h. The mixture was concentrated and the residue was extracted with petroleum ether. Concentration of the petroleum extracts left a solid which was crystallised from ethanol to give 1-(trimethylsilyl)-4-(triphenylsilyl)tetrafluorobenzene (3.6 g, 34.8%).

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