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VII*. PREPARATION AND REACTIONS OF (PENTACHLOROPHENYL)DIPHENYLCHLOROSILANE AND BIS(PENTACHLOROPHENYL)PHENYLCHLOROSILANE

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INTRODUCTION

Since the first reported preparations of pentachlorophenylmagnesium chloride[1] and pentachlorophenyllithium[2,2a] (I), the preparation and properties of a number of pentachlorophenyl-substituted silicon compounds have been described[2-7].

In a preliminary communication[4] we reported the preparation of two pentachlorophenyl-substituted silicon halides, namely tris(pentachlorophenyl)fluorosilane and bis(pentachlorophenyl)dichlorosilane. Unfortunately, it has so far been largely impossible to induce these two compounds to undergo reactions normally associated with organosilicon halides, such as hydrolyses to the corresponding silanols or siloxanes, reduction to the corresponding silanes, or coupling by metals to polysilanes.

We now wish to report the preparation and some reactions of two pentachlorophenyl-substituted phenylchlorosilanes: namely, (pentachlorophenyl)diphenylchlorosilane (II) and bis(pentachlorophenyl)phenylchlorosilane (III).

RESULTS AND DISCUSSION

Addition of (I) to an equimolar amount of dichlorodiphenylsilane in THF at $-65°$ resulted in a rapid replacement of one of the chlorine atoms of the chlorosilane to give (II) in 40% yield.

$$C_6Cl_5Li + ClSiPh_2Cl \xrightarrow[-65°]{THF} \underset{(II)}{C_6Cl_5SiPh_2Cl} + LiCl$$

By analogy with the above reaction it was expected that addition of (I) to phenyltrichlorosilane (mole ratio 1:1) under similar conditions should give pentachlorophenylphenyldichlorosilane. In fact when this reaction was carried out compound (III) was obtained in 10% yield. A similar reaction with a mole ratio of (I) to

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* For parts I–VI of this series see refs. 3–8.

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phenyltrichlorosilane of 2:1 gave (III) in 31.2% yield. However, when a ratio of (I) to phenyltrichlorosilane of 3:1 was employed, in an attempt to prepare tris(pentachlorophenyl)phenylsilane, an excess of (I) remained after the addition and was not consumed on prolonged stirring. The ratio of (I) to phenyltrichlorosilane was then adjusted to 2:1 by addition of more phenyltrichlorosilane. Almost immediately the unreacted (I) was consumed to give (III) in 17% yield:

$$\underset{2x\ \text{moles}}{C_6Cl_5Li} + \underset{2x\ \text{or}\ x\ \text{moles}}{PhSiCl_3} \xrightarrow[-65^\circ]{\text{THF}} \underset{\text{(III)}}{(C_6Cl_5)_2PhSiCl} + LiCl$$

Some hexachlorobenzene was isolated, in addition to (III), from the above reactions. As no hexachlorobenzene could be detected by VPC in a hydrolyzed sample of (I) it would appear that some halogen metal exhange must have occurred between (I) and phenyltrichlorosilane:

$$PhSiCl_3 + C_6Cl_5Li \rightarrow C_6Cl_6 + [PhSiCl_2Li]$$

Occurrence of a reaction of the above type would perhaps explain the relatively low yields of (III) obtained.

The fact that (III) was isolated from all reactions of (I) and phenyltrichlorosilane suggests that substitution of one pentachlorophenyl group into phenyltrichlorosilane activates a remaining chlorine atom thus facilitating disubstitution. However, as no tris(pentachlorophenyl)phenylsilane was obtained from reaction of (I) and phenyltrichlorosilane, it must be assumed that this activation is insufficient to overcome the steric requirements of placing three pentachlorophenyl groups and one phenyl group around a central silicon atom.

It is of interest to note that similar activation effects have been found in the preparation of certain pentafluorophenylsubstituted compounds. For instance, all attempts to prepare pentafluorophenyl-substituted silicon halides by reaction between a pentafluorophenylmetallic compound and silicon tetrachloride[9] or silicon tetrafluoride[4] have, so far, only given tetrakis(pentafluorophenyl)silane.

It is known that reaction of (I) with dichlorodiphenylsilane in a 2:1 molar ratio gives bis(pentachlorophenyl)diphenylsilane (IV) in moderate yields[10]. The fact that no (IV), could be detected, in addition to (II), from the reaction of (I) with dichlorodiphenylsilane in 1:1 molar ratio, probably again reflects the fact that any activating influence which the pentachlorophenyl group may have on the remaining chlorine atom, is overcome by steric restrictions. In marked contrast preliminary observations[10] indicate that the reaction of pentafluorophenyllithium with dichlorodiphenylsilane gives only bis(pentafluorophenyl)diphenylsilane and unreacted dichlorodiphenylsilane.

Compounds (II) and (III) were characterized by the normal analytical procedures and by acid hydrolysis to the corresponding silanols.

$$(C_6Cl_5)_nPh_{3-n}SiCl \xrightarrow{H_3O+} (C_6Cl_5)_nPh_{3-n}SiOH \qquad n = 1 \text{ or } 2$$

Hydrolysis of (II) and (III) under basic conditions gave pentachlorobenzene in good yields indicating that the pentachlorophenyl–silicon bond is susceptible to nucleophilic attack, as would be expected by analogy with pentafluorophenyl-substituted silicon compounds[11].

Treatment of (II) with lithium aluminum hydride in hot ether gave pentachlorophenyldiphenylsilane (V) in 27% yield, together with some pentachlorobenzene which was detected by VPC. Compound (V) was also prepared in 37% yield by the reaction between (I) and diphenylchlorosilane in THF at −65°. Compound (V) could simply be converted back to (II) in 35% yield, by treatment with chlorine in hot carbon tetrachloride.

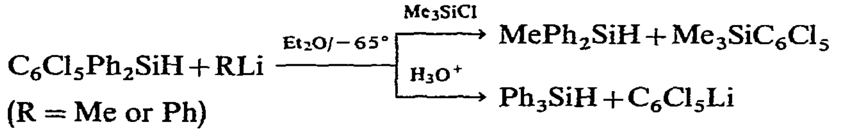
$$C_6Cl_5Ph_2SiCl \underset{Cl_2/CCl_4}{\overset{LiAlH_4/Et_2O}{\rightleftharpoons}} \underset{(V)}{C_6Cl_5Ph_2SiH} \xleftarrow[-65°]{THF} HPh_2SiCl + LiC_6Cl_5$$

All attempts to carry out a similar series of reactions with (III) were unsuccessful. After treatment of (III) with lithium aluminum hydride in hot ether for 24 hours much unreacted (III) was recovered. Treatment of (III) with lithium aluminum hydride in hot THF for 24 hours gave a small amount of pentachlorobenzene and a large amount of an intractable gum. The infrared spectrum of the latter material showed the presence of polychlorophenyl moities and also some weak carbon–hydrogen absorptions.

Attempts to prepare bis(pentachlorophenyl)phenylsilane, the expected reduction product of (III), by the reaction of (I) with phenyldichlorosilane in THF at −65° gave some hexachlorobenzene and an unidentified material, m.p. ~240°, which showed no silicon–hydrogen absorption in its infrared spectrum.

All attempts to prepare the known (pentachlorophenyl)triphenylsilane[5] by reaction of (II) or (III) with the stoichiometric amounts of phenyllithium, or phenylmagnesium bromide, in ether at room temperature have so far been unsuccessful.

Treatment of (V) with methyllithium in ether at −65° gave (I) and methyldiphenylsilane (37%). The presence of (I) in the reaction mixture was demonstrated by derivatization with chlorotrimethylsilane to give the known (pentachlorophenyl)-trimethylsilane in 29% yield. A similar reaction occurred between phenyllithium and (V); in this case triphenylsilane and pentachlorobenzene were identified by VPC subsequent to acid hydrolysis:



$$\begin{array}{l} C_6Cl_5Ph_2SiH + RLi \xrightarrow{Et_2O/-65°} \begin{cases} \xrightarrow{Me_3SiCl} MePh_2SiH + Me_3SiC_6Cl_5 \\ \xrightarrow{H_3O^+} Ph_3SiH + C_6Cl_5Li \end{cases} \\ (R = Me \text{ or } Ph) \end{array}$$

All attempts to prepare pentachlorophenyl-substituted polysilanes by reaction of (II) or (III) with metals in THF at room temperature have been unsuccessful. For instance, treatment of (II) with magnesium or lithium resulted in exothermic reactions and the formation of dark brown solutions which failed to give a positive color test[12] for organometallic species. Subsequent to the addition of chlorotrimethylsilane and acid hydrolysis, only small amounts of pentachlorobenzene could be isolated from the gummy reaction products. At this time it would appear that complex coupling involving both silicon–chlorine and carbon–chlorine bonds probably occurred in both cases.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. THF was dried over sodium followed by distillation from sodium benzophenone ketyl. Hexachlorobenzene was obtained from the Stauffer Chemical Co. The chlorosilanes used were from Dow Corning Corp., or Union Carbide Corp., and were used without further purification. n-Butyllithium in hexane and methyl- and phenyllithium in ether were from Foote Mineral. Unless otherwise stated molecular weight determinations were made in benzene using a Mechrolab vapor pressure osmometer, Model 201A. Infrared spectra were determined in carbon tetrachloride using a Perkin Elmer Model 21 spectrometer. All melting points are uncorrected.

Pentachlorophenyllithium

This compound was prepared as previously described[2a] by the addition of n-butyllithium in hexane to hexachlorobenzene suspended in THF at −65°. When it was necessary to add this material to a silicon halide, it was rapidly decanted under nitrogen into a jacketed addition funnel, cooled to −65° with dry ice and acetone.

Pentachlorophenyldiphenylchlorosilane

Pentachlorophenyllithium (0.05 mole) was added during 1 hour to dichlorodiphenylsilane (12.7 g, 0.05 mole) in THF (50 ml) at −65°. Immediately after the addition Color Test I[12] was negative. After warming to room temperature, the mixture was concentrated under nitrogen, treated with dry benzene and filtered under nitrogen to remove lithium chloride. The filtrate was concentrated and the residue recrystallized from dry petroleum ether (b.p. 60–80°) to give 9.4 g (40%) of product, m.p. 167–168°. (Found: Si, 6.12, 6.11; mol.wt., 458. $C_{18}H_{10}Cl_6Si$ calcd.: Si, 6.02%; mol.wt., 467.)

Reactions of pentachlorophenyllithium with phenyltrichlorosilane—preparation of bis-(pentachlorophenyl)phenylchlorosilane

(*a*) *Reactant ratio of* 1:1. Pentachlorophenyllithium (0.10 mole) was added to phenyltrichlorosilane (21.2 g, 0.1 mole) in THF (50 ml) at −65° during 1 h. Immediately after the addition Color Test I was negative. After warming to room temperature the mixture was concentrated, treated with dry benzene and filtered. Concentration of the benzene filtrate left a semi-solid which was treated with dry petroleum ether, to remove traces of a gummy material, filtered and the residue sublimed (120°/0.05 mm). The sublimate m.p. 227–230° was identified as hexachlorobenzene (4.3 g, 17.3%) by mixed melting point and comparison of its infrared spectra with an authentic sample. The sublimation residue was crystallized from dry petroleum ether (b.p. 90–100°) to give bis(pentachlorophenyl)phenylchlorosilane, m.p. 166–167°, 6.4 g (10%). [Found: Si, 4.66, 4.50; mol. wt. (mass spectrum), 640. $C_{18}H_5Cl_{10}Si$ calcd.: Si, 4.38%; mol.wt., 639.5.]

(*b*) *Reactant ratio of* 2:1. A similar reaction was carried out between pentachlorophenyllithium (0.1 mole) and phenyltrichlorosilane (10.6 g, 0.05 mole). Identical work-up to that previously described gave bis(pentachlorophenyl)phenylchlorosilane (11.5 g, 31.2%) and hexachlorobenzene (1.5 g, 5.25%).

(*c*) *Reactant ratio of* 3:1. Phenyltrichlorosilane (21.2 g, 0.10 mole) in THF

(50 ml) was added to pentachlorophenyllithium (0.30 mole) over 30 min. Color Test I remained positive after the addition and for the following 5 h. After this time more phenyltrichlorosilane (10.6 g, 0.05 mole) was added and Color Test I rapidly became negative. Work-up as previously described gave bis(pentachlorophenyl)phenylchlorosilane (16.3 g, 17%) and hexachlorobenzene (7.6 g, 8.9%).

Hydrolysis of (pentachlorophenyl)diphenylchlorosilane and bis(pentachlorophenyl)-phenylchlorosilane

(*a*) *Acidic conditions.* (Pentachlorophenyl)diphenylchlorosilane (4.4 g, 0.01 mole) was dissolved in THF (30 ml) and 1 *N* hydrochloric acid (10 ml) was added. The solution was stirred for 3 h. The organic layer was separated, dried, concentrated and the residue recrystallized from petroleum ether (b.p. 90–100°) to give (pentachlorophenyl)diphenylsilanol, m.p. 136–8°, 2.7 g (60%). [Found: Si, 6.41, 6.61; mol. wt. (mass spectrum), 448. $C_{18}H_{11}Cl_5OSi$ calcd.: Si, 6.27%; mol. wt., 448.5.] The infrared spectrum of this material showed an absorption at 3636 cm^{-1} characteristic of SiOH.

A similar reaction was carried out with 6.4 g (0.01 mole) of bis(pentachlorophenyl)phenylchlorosilane and gave bis(pentachlorophenyl)phenylsilanol, m.p. 182–184° (*ex* benzene). [Found: Si, 4.70, 4.40; mol. wt. (mass spectrum), 621. $C_{18}H_5Cl_{11}Si$ calcd.: Si, 4.51%; mol. wt., 621.0.] The infrared spectrum of this material also contained a characteristic SiOH absorption at 3649 cm^{-1}.

(*b*) *Basic conditions.* (Pentachlorophenyl)diphenylchlorosilane (4.4 g, 0.01 mole) was dissolved in THF (25 ml) and 10% sodium hydroxide (5 ml) was added. The solution was stirred for 3 h before the organic layer was separated, concentrated and recrystallized from methanol to give pentachlorobenzene (1.7 g, 68%). This compound was identified by mixed melting point and comparison of its infrared spectrum with an authentic sample.

A similar reaction with bis(pentachlorophenyl)phenylchlorosilane (3.2 g, 0.005 mole) gave 1.85 g (74%) of pentachlorobenzene.

(Pentachlorophenyl)diphenylsilane

(*a*) *By reduction of (pentachlorophenyl)diphenylchlorosilane with* $LiAlH_4$. (Pentachlorophenyl)diphenylchlorosilane (6.0 g, 0.013 mole) and $LiAlH_4$ were stirred in diethyl ether (50 ml) for 18 h. The mixture was then refluxed for 3 h when the ether was replaced by petroleum ether (b.p. 60–80°). The mixture was filtered, the filtrate concentrated and the residue recrystallized from hexane to give (pentachlorophenyl)-diphenylsilane, m.p. 93–94° (1.5 g, 27%). (Found: Si, 6.77, 6.74; mol. wt., 425. $C_{18}H_{11}Cl_5Si$ calcd.: Si, 6.49%; mol. wt., 432.6.) The infrared spectrum of this material contained a characteristic Si–H absorption at 2150 cm^{-1}.

(*b*) *By the reaction of pentachlorophenyllithium with diphenylchlorosilane* Pentachlorophenyllithium (0.05 mole) was added during 1 h to diphenylchlorosilane (10.9 g, 0.05 mole) in THF (50 ml). The mixture was allowed to attain room temperature overnight when it was concentrated. The silane (8 g, 37%) was isolated from the residue as described above.

Chlorination of pentachlorophenyldiphenylsilane

The silane (5.0 g, 0.0115 mole) was dissolved in carbon tetrachloride (150 ml) and the solution cooled to *ca.* −12°. Gaseous chlorine was passed slowly into the solution until an aliquot showed no Si–H absorption in its infrared spectrum. Nitrogen was then passed in to remove excess chlorine and then the solution was concentrated. Recrystallization of the residue from dry petroleum ether (b.p. 60–80°) gave pentachlorophenyldiphenylchlorosilane (1.9 g, 35 %) identified by mixed melting point with an authentic sample.

Reactions of (pentachlorophenyl)diphenylsilane

(*a*) *With methyllithium.* Methyllithium (0.01 mole) in ether was added to a solution of (pentachlorophenyl)diphenylsilane (4.5 g, 0.01 mole) in ether (50 ml) at −65°. The solution immediately turned red and Color Test I was still positive after 1 h. On addition of chlorotrimethylsilane (5 g, excess) the red color was discharged and Color Test I became negative. After warming to room temperature the solution was hydrolyzed by addition to dilute hydrochloric acid, the ethereal layer was separated, dried and concentrated. Distillation of the residue under reduced pressure gave methyldiphenylsilane b.p. 81–82°/0.15 mm, n_D^{20} 1.5689 lit.[13] b.p. 79°/0.1 mm, n_D^{20} 1.5694), 0.73 g (37 %). The identity of this material was further confirmed by comparison of its infrared spectrum with that of an authentic sample. The distillation residue was dissolved in benzene and chromatographed over alumina (Woelm neutral grade). Elution with petroleum ether (b.p. 60–80°) gave (pentachlorophenyl)trimethylsilane (0.95 g, 29.4 %) identified by mixed melting point with an authentic sample.

(*b*) *With phenyllithium.* A similar reaction was carried out with phenyllithium only in this case the mixture was hydrolyzed directly with acid. On examination by VPC (F and M Model 500 gas chromatograph, 1/4 × 18″ column packed with silicone gum rubber on chromosorb) pentachlorobenzene and triphenylsilane were identified.

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SUMMARY

The reaction of pentachlorophenyllithium (I) with dichlorodiphenylsilane at −65° gave (pentachlorophenyl)diphenylchlorosilane (II). A similar reaction of (I) with phenyltrichlorosilane in 1 : 1, 2 : 1 or 3 : 1 ratio gave bis(pentachlorophenyl)phenylchlorosilane (III). (II) and (III) were hydrolyzed under acidic conditions to the corresponding silanols. (II) was reduced by lithium aluminum hydride to (pentachlorophenyl)diphenylsilane (V). (V) was synthesized by reaction of (I) with diphenylchlorosilane and was converted back to (II) by treatment with chlorine in carbon tetrachloride. Treatment of (V) with an alkyl or aryllithium reagent at low temperature caused cleavage of the pentachlorophenyl group.

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