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POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS

VIII*. THE PREPARATION OF SOME PENTAFLUOROPHENYL-SUBSTITUTED ORGANOSILICON COMPOUNDS

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INTRODUCTION

Considerable interest has been shown recently in the preparation and properties of pentafluorophenyl derivatives of the elements[1]. However, relatively few derivatives of silicon have been reported. Tetrakis(pentafluorophenyl)silane[2,3], (pentafluorophenyl)trimethylsilane[4,5], methyl(pentafluorophenyl)diethoxysilane[6], bis(pentafluorophenyl)diethoxysilane[6], (pentafluorophenyl)dimethylsilane[6] and bis(pentafluorophenyl)methylsilane[6] were all prepared by the reaction of (pentafluorophenyl)-metallic compounds with the corresponding chlorosilanes. In addition (pentafluorophenyl)trimethylsilane[7] was obtained from the reaction of bromopentafluorobenzene with bis(trimethylsilyl)mercury, and dichlorofluoro(pentafluorophenyl)silane[5] and (pentafluorophenyl)trimethylsilane were obtained from the reactions of trichlorosilane and trimethylsilane with hexafluorobenzene under irradiation.

We now wish to report the preparation and some properties of the compounds $(C_6F_5)_nSiPh_{4-n}$ (where $n = 1$–4) and $(C_6F_5)_nPh_{3-n}SiX$ (where $n = 1$ or 2 and $X = H$ or Cl).

RESULTS AND DISCUSSION

Initial attempts were made to prepare (pentafluorophenyl)triphenylsilane (I) by the reaction of pentafluorophenylmagnesium bromide with chlorotriphenylsilane in ether. Even after refluxing the reaction mixture for six hours only unreacted chlorotriphenylsilane was isolated. Similarly the reaction of pentafluorophenyllithium with chlorotriphenylsilane in ether at −65° gave no detectable products and much unreacted chlorotriphenylsilane was again isolated after the reaction mixture had been warmed to room temperature.

Pentafluorophenyllithium in THF did not react with chlorotriphenylsilane to any appreciable extent at −65° as shown by VPC. However, on warming the reaction mixture to 20° during three hours all the organometallic compound was consumed to give a mixture of products, from which was isolated compound (I) (12%), fluorotri-

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phenylsilane (14%) and a large amount of material which did not melt below 450°, although it softened at 350–400°, depending on the sample. The latter material was insoluble in dilute acid and most common organic solvents. The infrared spectrum of this material (in KBr) contained absorptions characteristic of silicon–phenyl and polyfluorophenyl moities. Although conclusive evidence is lacking for this statement the material will be referred to as a "polymer".

Some support for the above statement was provided by the work of Tamborski *et al.*[8], who showed that compounds of the form $C_6F_5(C_6F_4)_nC_6F_5$ were formed, in addition to tetrakis(pentafluorophenyl)silanes, during the reaction of pentafluorophenylmagnesium bromide with silicon tetrachloride in THF. It thus appears that during the preparation of compound (I) appreciable decomposition of the pentafluorophenyllithium may have occurred to give a "polymer", possibly with the elimination of lithium fluoride. If this was so, then the fluorotriphenylsilane which was isolated could have arisen as follows:

$$Ph_3SiCl + LiF \rightarrow Ph_3SiF + LiCl$$

Similar yields of compound (I) (12.5%), fluorotriphenylsilane (14%) and "polymer" were obtained from the reaction of pentafluorophenylmagnesium bromide with chlorotriphenylsilane in THF. In this case the reaction only proceeded to an appreciable extent on heating the mixture to reflux for some hours.

The apparent reluctance of (pentafluorophenyl)metallic compounds to react with chlorotriphenylsilane is of interest for under similar conditions, pentachlorophenylmagnesium chloride[9] and pentachlorophenyllithium[10] react rapidly with chlorotriphenylsilane to give good yields of (pentachlorophenyl)triphenylsilane. This suggests that under the conditions used the (pentafluorophenyl)metallic compounds were less reactive than the corresponding (pentachlorophenyl)metallic compounds.

In an attempt to improve the yield of compound (I) the reaction of pentafluorophenyllithium in THF with bromotriphenylsilane was investigated. This reaction proceeded to completion at −65° giving compound (I) in fair yield (48.4%) with the formation of much less fluorotriphenylsilane and polymer than was obtained from a comparable reaction of chlorotriphenylsilane.

One other route to compound (I) was examined, the reaction of triphenylsilyllithium with hexafluorobenzene. The reaction was initially carried out by the slow addition of triphenylsilyllithium (x moles) in THF to hexafluorobenzene ($4x$ moles) in THF at −65°. A rapid reaction occurred but no compound (I) could be detected among the products. However, the reaction is of considerable interest because a major product was 1,4-bis(triphenylsilyl)tetrafluorobenzene. The results of this and similar investigations will be published at a later date.

Bis(pentafluorophenyl)diphenylsilane (II) and tris(pentafluorophenyl)phenylsilane (III) were obtained in 48.5 and 50% yields by the addition of diphenyldichlorosilane and phenyltrichlorosilane, respectively, in ether to pentafluorophenyllithium in ether at −65°. However, the reactions were still slow and did not proceed to completion until warmed to room temperature.

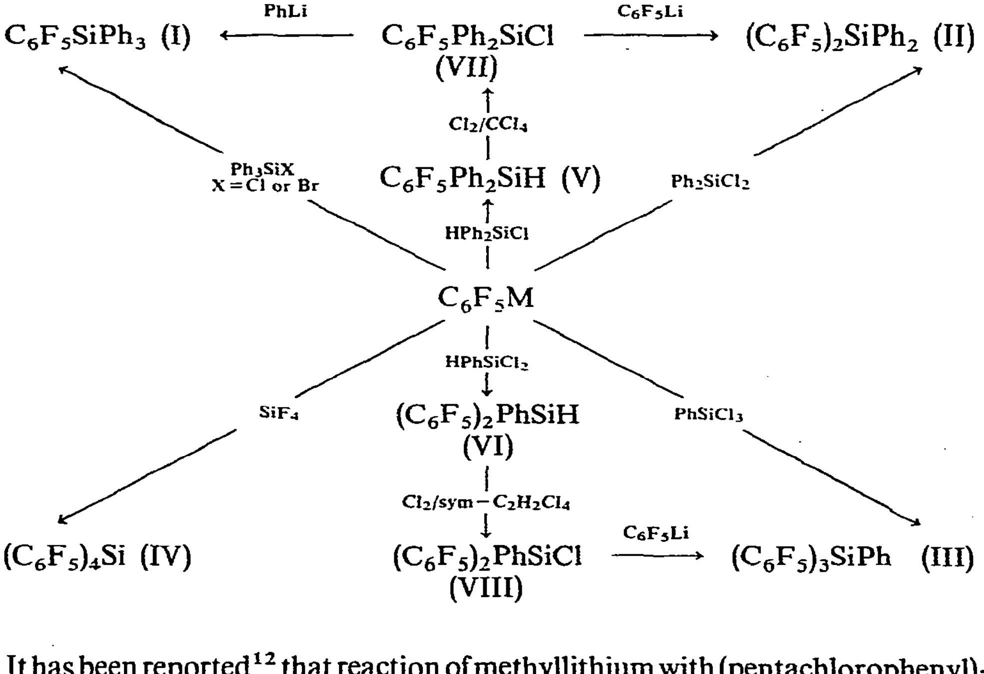
In a preliminary communication[11], we mentioned that tetrakis(pentafluorophenyl)silane (IV) had been obtained in 48.7% yield by the reaction of silicon tetrafluoride with pentafluorophenylmagnesium bromide in ether at room temperature. The details of this reaction are now reported in the experimental section.

(Pentafluorophenyl)diphenylsilane (V) was prepared in 71.5% yield by the addition of diphenylchlorosilane in ether to pentafluorophenyllithium in ether at −65°. A similar reaction with phenyldichlorosilane gave bis(pentafluorophenyl)phenylsilane (VI) in 41% yield.

Compound (V) was converted to (pentafluorophenyl)diphenylchlorosilane (VII) in 75.9% yield by treatment with chlorine in refluxing carbon tetrachloride during four hours. When a similar reaction was carried out with compound (VI), little reaction appeared to occur during six hours. However, treatment of compound (VI) with chlorine in the higher boiling sym-tetrachloroethane gave bis(pentafluorophenyl)phenylchlorosilane (VIII) in 87% yield.

An attempt was made to prepare compound (VII) directly by the slow addition of pentafluorophenyllithium (x moles) in ether to diphenyldichlorosilane (x moles) in ether at −65°. Only compound (II) (38%) and unreacted diphenyldichlorosilane (48%) were isolated, a fact which appears to provide further support for the statement[2] that attachment of a pentafluorophenyl group to silicon activates a remaining silicon–halogen bond to nucleophilic attack by a (pentafluorophenyl)metallic compound. In marked contrast, it has been reported[12] that under similar conditions pentachlorophenyllithium in THF gave a 40% yield of (pentachlorophenyl)diphenylchlorosilane.

Compound (VII) was converted into compound (I) in 60.1% yield by treatment with phenyllithium in ether at −65°. Treatment of compound (VII) with pentafluorophenyllithium in ether gave compound (II) in 62.5% yield and a similar reaction between compound (VIII) and pentafluorophenyllithium in ether gave compound (III) in 57.8% yield. The reactions described so far are summarized by the following scheme and by Table 1.



It has been reported[12] that reaction of methyllithium with (pentachlorophenyl)diphenylsilane in THF at −65° resulted in cleavage of the pentachlorophenyl group

TABLE 1

METHODS OF PREPARATION OF VARIOUS PENTAFLUOROPHENYL-SUBSTITUTED SILICON COMPOUNDS

Compound	*M.p. or b.p. and n_D^{20}*	*Reactants*	*Solvent*	*Yield (%)*	*Other products (%)*
$Ph_3SiC_6F_5$ (I)	129–130°	$C_6F_5MgBr + Ph_3SiCl$	Et_2O	0	unreacted Ph_3SiCl
		$C_6F_5Li + Ph_3SiCl$	Et_2O	0	unreacted Ph_3SiCl
		$C_6F_5MgBr + Ph_3SiCl$	THF	13.5	Ph_3SiF (14), "polymer"
		$C_6F_5Li + Ph_3SiCl$	THF	12.0	Ph_3SiF (19.8), "polymer"
		$C_6F_5Li + Ph_3SiBr$	THF	48.4	Ph_3SiF (5.3), "polymer"
		$PhLi + C_6F_5Ph_2SiCl$	Et_2O	76.4	
$Ph_2Si(C_6F_5)_2$ (II)	151–152°	$2\ C_6F_5Li + Ph_2SiCl_2$	Et_2O	48.5	
		$C_6F_5Li + C_6F_5Ph_2SiCl$	Et_2O	62.5	
$PhSi(C_6F_5)_3$ (III)	136–137°	$3\ C_6F_5Li + PhSiCl_3$	Et_2O	50.0	
		$C_6F_5Li + (C_6F_5)_2PhSiCl$	Et_2O	57.8	
$(C_6F_5)_4Si$ (IV)	246–247°	$C_6F_5MgBr + SiF_4$	THF	47.0	
$C_6F_5Ph_2SiH$ (V)	39–40° 130–132°/0.07 mm	$C_6F_5Li + ClPh_2SiH$	Et_2O	71.6	
$(C_6F_5)_2PhSiH$ (VI)	109°/0.07 mm 1.5193	$2\ C_6F_5Li + Cl_2PhSiH$	Et_2O	41.0	
$C_6F_5Ph_2SiCl$ (VII)	140–141°/0.6 mm	$C_6F_5Ph_2SiH + Cl_2$	CCl_4	75.9	
	1.5591	$C_6F_5Li + Ph_2SiCl_2$	Et_2O	0	$(C_6F_5)_2SiPh_2$ (38.0), Ph_2SiCl_2 (48.0)
$(C_6F_5)_2PhSiCl$ (VIII)	124–125°/0.05 mm 1.5270	$(C_6F_5)_2PhSiH + Cl_2$	sym- $C_2H_2Cl_4$	87.0	

from silicon to give pentachlorophenyllithium and methyldiphenylsilane (37%). Chlorotrimethylsilane was used in this reaction to trap the pentachlorophenyllithium as (pentachlorophenyl)trimethylsilane in 29% yield:

$$C_6Cl_5Ph_2SiH + MeLi \xrightarrow[-65^{\circ}]{THF} C_6Cl_5Li + MePh_2SiH$$
$$\xrightarrow{Me_3SiCl} C_6Cl_5SiMe_3$$

A similar reaction was carried out between compound (V) and methyllithium. In this case a rapid reaction occurred, all the compound (V) being consumed within 15 minutes, to give methyldiphenylsilane (60.5%) and (pentafluorophenyl)trimethylsilane (44%) subsequent to derivatization with chlorotrimethylsilane, indicating that the pentafluorophenyl group had been cleaved from silicon as follows:

$$\underset{(V)}{C_6F_5Ph_2SiH} + MeLi \xrightarrow[-65^{\circ}]{THF} C_6F_5Li + MePh_2SiH$$
$$\xrightarrow{Me_3SiCl} C_6F_5SiMe_3$$

A similar reaction was carried out with n-butyllithium to give (pentafluorophenyl)trimethylsilane (41.7%) and n-butyldiphenylsilane (55.7%):

$$\underset{(V)}{C_6F_5Ph_2SiH} + n\text{-}BuLi \xrightarrow[-65^{\circ}]{THF} C_6F_5Li + BuPh_2SiH$$
$$\xrightarrow{Me_3SiCl} C_6F_5SiMe_3$$

From the above reaction a low yield of a third product was isolated in an impure state. The nuclear magnetic resonance spectrum of this material contained the following characteristic absorptions: phenyl (τ 2.65 ppm), silicon-hydrogen (τ 4.35 ppm) and n-butyl (τ 7.3, 8.5 and 9.05 ppm), the integrated area ratio being 9.8 : 1.0 : 8.9. The mass spectrum of this material indicated a molecular weight of 389.0. On the basis of this evidence the material would appear to be a product of n-butyl substitution in the pentafluorophenyl ring of compound (V).

$$\underset{(V)}{C_6F_5Ph_2SiH} + n\text{-}BuLi \rightarrow n\text{-}BuC_6F_4Ph_2SiH + LiF$$

Such a product would require a molecular weight of 388.3 and an integrated area ratio of 10.0 : 1.0 : 9.0.

Numerous reactions were carried out between compound (VII) and metals in various solvents, in attempts to obtain a pentafluorophenyl-substituted silylmetallic compound. However, in no case was any identifiable product obtained. For instance, compound (VII) reacted rapidly with lithium in THF at −65° to give a highly colored solution which contained no organometallic species. Work-up gave a yellow gum, the infrared spectrum of which indicated the presence of polyfluorophenyl and phenyl groups attached to silicon. In view of the evidence that we are currently obtaining about the reactivity of silyllithium compounds towards hexafluorobenzene, it appears that if a pentafluorophenyl-substituted silylmetallic compound had been formed during the above reaction, it would have probably attacked a pentafluorophenyl ring, resulting, presumably, in the formation of polymeric products.

Physical properties

(*a*) *Infrared spectra.* The infrared spectrum of compound (IV) was reported[3] to be characterized by the following absorptions: 1641 (m), 1516 (s), 1466 (s), 1379 (s), 1292 (s), 1140 (w), 1098 (s), 1023 (w), and 970 (s) cm^{-1}. The infrared spectra of all of the compounds prepared in this work were characterised by similar absorptions within the limits ±10 cm^{-1}, the intensity of these absorptions being directly related to the number of pentafluorophenyl groups attached to the silicon atom. All of the compounds prepared, with the exception of compound (IV), also contained phenyl groups attached to silicon, thus the spectra also contained the characteristic absorptions of phenyl attached to silicon[13]. Compounds (V) and (VI) showed characteristic silicon–hydrogen absorptions at 2018 and 2020 cm^{-1} respectively.

(*b*) *Ultraviolet spectra.* The ultraviolet spectra of the compounds (I), (II), (III) and (IV), *i.e.* the series $(C_6F_5)_nSiPh_{4-n}$, were recorded in cyclohexane. The absorptions are summarised in Table 2. As the phenyl groups were replaced by pentafluorophenyl groups the extinction coefficient increased in a fairly uniform manner. It was also observed that whereas compound (I) showed a typical benzenoid fine structure pattern[14] between 250 and 270 mμ, the fine structure was gradually suppressed as the number of pentafluorophenyl groups was increased, until, in the case of compound (IV) only one broad absorption was present centered around 271 mμ. All of the spectra also contained a shoulder at *ca.* 220 mμ. However, this shoulder was too indistinct for precise measurements to be made.

TABLE 2

ULTRAVIOLET SPECTRAL DATA OF THE COMPOUNDS $(C_6F_5)_nSiPh_{4-n}$[a]

Compound *n*	*Band position* *max (mμ)*	*Molar absorptivity* *ε*
1	270.5, 265.5, 260.5, 254.5[b]	1716, 2068, 1760, 1210
2	273, 267.5, 261.5[b]	2687, 3115, 2570
3	271.5[b], 265.5, 261.5[b]	3738, 3951, 3096
4	271	4720

[a] Obtained with a Beckman OK-2A spectrophotometer using cyclohexane as solvent. [b] Shoulder.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. Ethereal solvents were dried over sodium, THF was further purified by distillation from sodium–benzophenone ketyl. Pentafluorobenzene and bromopentafluorobenzene were obtained from Imperial Smelting and were dried over phosphorus pentoxide before use. n-Butyllithium in hexane, methyllithium in ether and phenyllithium in ether/benzene were obtained from Foote Mineral. Organosilicon halides, except for bromotriphenylsilane and silicon tetrafluoride, were obtained from Dow Corning and were used without further purification. Bromotriphenylsilane was prepared by the bromination of triphenylsilane[15]. Silicon tetrafluoride was obtained from Matheson. Petroleum ether had a b.p. of 60–70°. Alumina was Woelm neutral grade. Infrared spectra were determined in KBr (solids) or as capillary films (liquids) using a Perkin Elmer Model 21 spectrometer. Molecular weights were determined by mass spectrometry. VPC analyses were carried out with an F and M Model 500 Gas Chromotograph using an 18 × $\frac{1}{4}''$ column packed with silicon gum rubber, SE 30, on Chromosorb W (1 : 20). All melting points are uncorrected.

(Pentafluorophenyl)metallic compounds

Pentafluorophenyllithium[16] was prepared in either ether or THF, by the addition of a solution of pentafluorobenzene in ether or THF, to an equimolar amount of n-butyllithium in hexane.

Pentafluorophenylmagnesium bromide[3] was prepared in THF by addition of bromopentafluorobenzene in THF to a slight excess of magnesium turnings.

The preparation of (pentafluorophenyl)triphenylsilane, (I), by the reaction of (pentafluorophenyl)metallic compounds with halotriphenylsilanes

(*a*) *Pentafluorophenyllithium and chlorotriphenylsilane in THF.* Chlorotriphenylsilane (29.45 g, 0.1 mole) in THF (100 ml) was added to a solution of pentafluorophenyllithium (0.1 mole) in THF (150 ml) at −65°. The mixture was stirred for 6 h at −65° when Color Test I[17] was still positive and VPC showed the presence of much unreacted chlorotriphenylsilane. The mixture was allowed to warm to 20° during 3 h when Color Test I was negative. The reaction mixture was filtered to give 13.0 g of a waxy solid, which did not melt below 430°. The THF filtrate was concentrated and the residue dissolved in benzene, filtered, the benzene filtrate was concentrated and the residue distilled under reduced pressure to remove fluorotriphenylsilane: b.p. 143–147°/0.3 mm, m.p. 61–62°, (5.5 g 19.8 %). This material was identical in all respects to an authentic sample. The distillation residue was dissolved in petroleum ether and chromotographed over alumina. Elution with petroleum ether gave a white solid which was crystallised from pentane at −30° to give compound (I), m.p. 129–130° (5.1 g 12%). (Found: C, 68.1, H; 3.54; F, 21.9; mol. wt., 426. $C_{24}H_{15}F_5Si$ calcd.: C, 68.08; H, 3.52; F, 22.28%; mol. wt., 426.3.)

(*b*) *Pentafluorophenylmagnesium bromide and chlorotriphenylsilane in THF.* Chlorotriphenylsilane (14.7 g, 0.05 mole) in THF (50 ml) was added to a solution of pentafluorophenylmagnesium bromide (0.05 mole) in THF (100 ml). After 2 h stirring at room temperature no compound (I) could be detected by VPC, so the mixture was refluxed for 6 h. After this time Color Test I was negative. The mixture was worked up as described above to give 7.7 g of infusible material, fluorotriphenylsilane (2.0 g, 14.4%) and compound (I) (2.9 g, 13.5%).

(*c*) *Pentafluorophenyllithium and bromotriphenylsilane in THF.* Bromotriphenylsilane (16.95 g, 0.05 mole) in THF (100 ml) was added to pentafluorophenyllithium (0.05 mole) in THF (100 ml) at −65°. After 3 h stirring at this temperature Color Test I was negative. Similar workup to that described above gave 2.3 g of the infusible solid, fluorotriphenylsilane (0.74 g, 5.3%) and compound (I) (10.3 g, 48.4%).

Bis(pentafluorophenyl)diphenylsilane, (II), from pentafluorophenyllithium and diphenyldichlorosilane

Diphenyldichlorosilane (12.65 g, 0.05 mole) in ether (50 ml) was added to pentafluorophenyllithium (0.1 mole) in ether (100 ml) The solution was stirred for 6 h at −65° when Color Test I was still slightly positive. The mixture was warmed to 20°, concentrated, the residue extracted with petroleum ether and chromatographed over alumina. Elution with petroleum ether gave a white solid which was crystallised from pentane to give compound (II), m.p. 151–152° (12.5 g, 48.5%). (Found: C, 55.9; H, 1.98; F, 36.1; mol. wt., 516. $C_{24}H_{10}F_{10}Si$ calcd.: C, 55.82; H, 1.93; F, 36.81%; mol. wt., 516.3.)

Tris(pentafluorophenyl)phenylsilane, (III), from pentafluorophenyllithium and phenyltrichlorosilane

Phenyltrichlorosilane (10.6 g, 0.05 mole) in ether (50 ml) was added to pentafluorophenyllithium (0.15 mole) in ether (150 ml) at −65°. After 5 h stirring Color Test I was negative. The reaction mixture was warmed to 20°. Compound (III) was isolated in a similar manner to compound (II), as a white solid, m.p. 136–137° (15.0 g, 50%). (Found: C, 47.7; H, 0.99; F, 47.9; mol. wt., 606. $C_{24}H_5F_{15}Si$ calcd.: C, 47.53; H, 0.82; F, 47.00%; mol. wt., 606.3.)

Tetrakis(pentafluorophenyl)silane, (IV), from silicon tetrafluoride and pentafluorophenylmagnesium bromide

Silicon tetrafluoride was passed into a solution of pentafluorophenylmagnesium bromide (0.1 mole) in THF (150 ml) at room temperature until Color Test I was negative. The reaction mixture was concentrated and the residue extracted with hot benzene. The benzene extracts, after concentration and cooling gave compound (IV), m.p. 246–247° (8.2 g, 47%). This material was identical to an authentic sample (kindly supplied by Dr. C. Tamborski).

Pentafluorophenyldiphenylsilane, (V), from pentafluorophenyllithium and diphenylchlorosilane

Diphenylchlorosilane (22.0 g, 0.1 mole) in ether (50 ml) was added to pentafluorophenyllithium (0.1 mole) in ether (100 ml) at −65°. Color Test I was negative after 6 h stirring at −65°. The mixture was warmed to room temperature, concentrated, the residue extracted with petroleum ether and filtered. The filtrate was concentrated and the residual liquid distilled under reduced pressure to give compound (V) (25.1 g 71.6%), b.p. 130–132°/0.1 mm, n_D^{20} 1.5591. (Found: C, 61.6; H, 3.19; F, 27.1; mol. wt., 350. $C_{18}H_{11}F_5Si$ calcd.: C, 61.71; H, 3.14; F, 27.11%; mol. wt., 350.3.)

Bis(pentafluorophenyl)phenylsilane, (VI), from pentafluorophenyllithium and phenyldichlorosilane

Phenyldichlorosilane (8.8 g, 0.05 mole) in ether (50 ml) was added to pentafluorophenyllithium (0.1 mole) in ether (100 ml) at −65°. Color Test I was negative after 12 h stirring at −65°. Compound (VI) was isolated in a similar manner to compound (V) (9.1 g, 41.4%) b.p. 109–110°/0.07 mm, n_D^{20} 1.5193. (Found: C, 49.6; H, 1.36, F, 42.8; mol. wt., 440. $C_{12}H_6F_{10}Si$ calcd.: C, 49.10; H, 1.36; F, 43.15%; mol. wt., 440.3.)

(Pentafluorophenyl)diphenylchlorosilane, (VII), by treatment of compound (V) with chlorine in carbon tetrachloride

Compound (V) (20.0 g, 0.057 mole) was dissolved in hot carbon tetrachloride (150 ml) and chlorine was passed into the refluxing solution. After 3 h no unreacted starting material could be detected by VPC. The solution was concentrated under nitrogen and the residue distilled under reduced pressure to give compound (VII) (16.7 g, 75.9%), b.p. 140–149/0.6 mm, n_D^{20} 1.5591. (Found: C, 56.4; H, 2.8; Cl, 9.4; F, 24.9; mol. wt., 385. $C_{18}H_{10}ClF_5Si$ calcd.: C, 56.18; H, 2.60; Cl, 9.22; F, 24.69%; mol. wt., 384.9.)

Attempted preparation of compound (VII) by a direct reaction between pentafluorophenyllithium and diphenyldichlorosilane

Pentafluorophenyllithium (0.05 mole) in ether (50 ml) at −65° was added dropwise with stirring to diphenyldichlorosilane (12.5 g, 0.05 mole) in ether (50 ml) at −65°. Color Test I was negative immediately after the addition when VPC indicated that no compound (VII) was present. The mixture was concentrated and distilled under reduced pressure to give unreacted diphenyldichlorosilane (6.0 g, 48%). The distillation residue was recrystallised from pentane to give compound (II), m.p. 149–151° (4.86 g, 38%).

Bis(pentafluorophenyl)phenylchlorosilane, (VIII), by treatment of compound (VI) with chlorine in sym-tetrachloroethane

Compound (VI) (10.0 g, 0.028 mole) was dissolved in hot sym-tetrachloroethane (100 ml). Chlorine was passed into the refluxing solution. After 3 h no unreacted starting material could be detected by VPC. The solution was concentrated under nitrogen and the residue distilled under reduced pressure to give compound (VIII) (9.5 g, 87%), b.p. 124–125°/0.05 mm., n_D^{20} 1.5270. (Found: C, 45.8; H, 0.98; Cl, 7.7; Si, 5.6; mol. wt., 475. $C_{18}H_5ClF_{10}Si$ calcd.: C, 45.54; H, 1.05; Cl, 7.48; Si, 5.92%; mol. wt., 474.8.)

Reaction of compound (VII) with phenyllithium

Compound (VII) (3.0 g, 0.078 mole) in ether (25 ml) was cooled to −65° and phenyllithium (0.078 mole) in ether (25 ml) was added. After stirring for 1 h Color Test I was negative. The mixture was concentrated, the residue extracted with petroleum ether and the extracts chromatographed over alumina. Elution with petroleum ether gave a white solid which was recrystallised from pentane to give compound (I), m.p. 129–130° (2.5 g, 76.4%).

Reaction of compounds (VII) and (VIII) with pentafluorophenyllithium

Pentafluorophenyllithium (0.078 mole) in ether (25 ml) was added to compound VII (3.0 g, 0.078 mole) in ether (25 ml) at −65°. Color Test I was negative after 3 h. Identical work-up to that described above gave compound (II), m.p. 149–151° (2.5 g, 62:5%).

A similar reaction was carried out between compound (VIII) (4.75 g, 0.01 mole) and pentafluorophenyllithium (0.01 mole) to give compound (III), m.p. 137–139° (3.5 g, 57.8%).

Reaction of compound (V)

(*a*) *With methyllithium.* Methyllithium (0.02 mole) in ether (15 ml) was added to a solution of compound (V) (7.0 g, 0.02 mole) in THF (50 ml) at −65°. The solution immediately turned purple and after 15 min VPC showed that no (V) remained. However, Color Test I was still positive. Chlorotrimethylsilane (0.03 mole) was added and Color Test I was immediately negative. The reaction mixture was allowed to warm to room temperature, filtered and the solvents removed by distillation through a short Vigreaux column. The residual oil was distilled under reduced pressure to give (pentafluorophenyl)trimethylsilane (2.1 g, 44%), b.p. 61–62°/14 mm, n_D^{20} 1.4315 (lit.[3] b.p. 60°/14 mm, n_D^{20} 1.4331), and methyldiphenylsilane (2.4 g, 60.5%), b.p. 82–83°/0.5 mm, n_D^{20} 1.5701 (lit.[18] b.p. 79°/0.1 mm, n_D^{20} 1.5694). The identity of these two compounds was confirmed by comparison of their infrared spectra with authentic materials.

(*b*) *With n-butyllithium.* A similar reaction was carried out between compound (V) (10.5 g, 0.03 mole) and n-butyllithium (0.03 mole). The reaction mixture again turned purple and all of compound (V) was consumed during 15 min. Chlorotrimethylsilane (0.04 mole) was added and the reaction mixture was worked up as described above to give (pentafluorophenyl)trimethylsilane (3.0 g, 41.7%) b.p. 63–64°/15 mm, n_D^{20} 1.4317 and n-butyldiphenylsilane (4.1 g, 55.7%), b.p. 102–105°/0.6 mm, n_D^{20} 1.5520 (lit.[18] 110–112°/1 mm, n_D^{20} 1.5541). In addition, 2.8 g of a liquid b.p. 147–150°/0.15 mm was obtained. Spectral evidence, presented in the discussion, suggests that this material was principally a compound formed by n-butyl-substitution in the pentafluorophenyl ring of compound (V).

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SUMMARY

The preparation and some properties of the compounds $(C_6F_5)_nSiPh_{4-n}$ (where $n = 1$–4) and $(C_6F_5)_nPh_{3-n}SiX$ (where $n = 1$ or 2 and X = H or Cl) are described. In general, these compounds were obtained by the reaction of a (pentafluorophenyl)-metallic compound with the corresponding chlorosilane. However, compounds of the form $(C_6F_5)_nPh_{3-n}SiCl$ could not be obtained in this manner; they were prepared by the chlorination of the corresponding organosilicon hydrides.

Evidence is presented which suggests that pentachlorophenyllithium is more reactive towards chlorotriphenylsilane than is pentafluorophenyllithium under similar conditions.

The reaction of an alkyllithium compound with (pentafluorophenyl)diphenylsilane leads predominantly to cleavage of the pentafluorophenyl group from silicon.

The infrared spectra of all the above compounds are discussed and the ultraviolet spectra of the compounds $(C_6F_5)_nSiPh_{4-n}$ (where $n = 1$–4) are reported.

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