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ORGANOMETALLIC AND ORGANOMETALLOIDAL HIGH–TEMPERATURE LUBRICANTS AND RELATED MATERIALS

HENRY GILMAN, et al.

IOWA STATE UNIVERSITY

TECHNICAL REPORT AFML-TR-64-383, Part IV

DECEMBER 1967

Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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50th Anniversary
1917 1967
Materials Research in the Air Force

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NOTICES

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FOREWORD

This report was prepared by Iowa State University of Science and Technology, Ames, Iowa, under USAF Contract No. AF 33(615)-2368. The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena", Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials". The work was administered under the direction of the Air Force Materials Laboratory with Dr. Christ Tamborski and Dr. William L. Respess acting as project engineers.

This report covers work reported from 15 December, 1966 to 15 December, 1967. The authors are: Henry Gilman, Thomas Brennan, S. S. Dua, F. W. G. Fearon, A. E. Jukes, Peter J. Morris, and Kyo Shiina.

Report was submitted by authors December 1967.

This technical report has been reviewed and is approved.

William E. Gibbs

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ABSTRACT

The primary objective of our studies is the preparation of useful, thermally stable fluids, lubricants, etc. This has involved the synthesis of compounds containing units having particularly a plurality of fluorine atoms, as well as some having a plurality of chlorine atoms. These as well as the silicon atoms contained in many of the compounds should provide monomers having reactive functional groupings to give access to novel thermally stable polymers. Among the polyfluoro types being studied are those containing a bridge such as $-(CF_2)_n-$.

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I. INTRODUCTION

The objective of these studies is the preparation and determination of chemical and physical properties of organometallic and organometalloidal compounds containing primarily polyfluoro substituents, as well as polychloro groups. Into these monomeric compounds are being introduced two or more functional groups to provide ready access to novel polymers, which will have appropriately useful properties such as high thermal stabilities, for use in fluids, lubricants, etc. Among the current types being examined are those having not only polyhalogenated substituents (which are known generally to impart enhanced thermal stability), but also organosilicon groupings. The organosilicon types have long been known to improve thermal stabilities.

We started this amended course of our original objective with the more accessible and less expensive (and yet promising for increasing thermal stability) polychloro types having four or five chlorine atoms in a given substituent or R group. Then we included to an increasing degree the analogous polyfluoro aromatic substituents. The next stage has involved studies on polyfluorinated alkanes having units such as: $-(CF_2)_n-$

Among the compounds described at this time are those having structures like the following: $C_6X_5(SiMe_2)_nC_6X_5$. Compounds such as these are readily available from the reaction of C_6X_5M compounds and $X-(Me_2Si)_n-X$ (a series described in our earlier reports). The polyhalophenyl-dimethylsilanes, $C_6X_5(Me_2Si)_nC_6X_5$, have a chief interest as possible intermediates to the di-metallic species which can then be used to make highly reactive monomers. For example, the following selected series of transformations should provide the terminal di-functional compound having two Si-Cl linkages which should be readily convertible to polymers having the disiloxane units

$C_6X_5SiMe_2C_6X_5 \longrightarrow$ *p*-$M-C_6X_4SiMe_2C_6X_4-M \longrightarrow$
p-$ClSiMe_2C_6X_4SiMe_2C_6X_4SiMe_2Cl \longrightarrow$ disiloxane and other polymers. In such a generalized representation the terminal $ClSiMe_2-$ groups can be replaced by other reactive functional groups such as $HSiMe_2-$ which retain the valuable property of so-called conventional polymer formation and also expand the number of opportunities for varied polymer formation by their capacity to add to unsaturated systems.

Among the more versatile and reactive compounds are the silylmetallics, R_3SiM. Actually, some of these compounds are not only more reactive but also more versatile than the widely used Grignard reagents and organolithium compounds. In the generalized formula R_3SiM, lithium is frequently the M component or metal. It is interesting to note that extremely little is known of the sodium analogs, R_3SiNa. In order to obtain a greater versatility of reaction, based on some selectivity, we have developed convenient and useful procedures for the preparation of R_3SiNa types. In this connection, the marked success in the preparation and reactions of compounds such as:

$M-(SiPh_2)_n-M$ suggested a like series of syntheses leading to types wherein the Ph groups are replaced by C_6X_5 groups. However, these and related promising types have not so far been made. Accordingly, we have examined a series of stepwise reactions concerned with R_3SiM types leading to combinations containing C_6X_5 and C_6H_5 groups. Some reactions involving transformations of RRSiHCl are described. Regrettably there appears no great promise for silyl-metallic compounds of the following generalized types, in which the R groups are perhalogenated: R_3SiM and $M-(R_2Si)_n-M$ Fortunately, there are other approaches both indicated, and found, involving intermediately the use of accessible silylmetallic types for the realization of the objectives of this project.

One of the types of special interest is the following:

$$\underline{p}\text{-}HMe_2Si\text{-}C_6F_4(CF_2)_nC_6F_4SiMe_2H\text{-}\underline{p}$$

Here experiments are described which are applicable to a highly fluorinated monomer containing silicon, and more than one reactive functional group to provide access to polymers. Incidental to the preparation of compounds of this type, as well as a wide variety of other important compounds, is a di-metallic compound such as:

$$M-(CF_2)_n-M$$

It now appears that a simple metalloidal type such as the following might be made for polymer formation:

$$(HMe_2Si)_3Si(CF_2)_nSi(SiMe_2H)_3$$

This and an even simpler analog such as: $HMe_2Si(CF_2)_nSiMe_2H$, should give ready access to highly fluorinated (or highly chlorinated or a combination of the two) compounds by addition to some polyhalogenated unsaturated systems.

We have emphasized the primary importance of the polyfluorinated types. Of secondary importance are the polychlorinated compounds. Some useful guide-lines to the polyfluoro compounds are derivable from the other polyhalogen types, in addition to their intrinsic value in studies on the preparation of useful monomers leading to polymers with appropriate thermal characteristics. We mention that such compounds may not only be of some value in themselves, but may provide novel and important starting materials. A case in point is the conversion of hexabromobenzene to the interesting hexakis(hydrodimethylsilyl)benzene: $C_6(Me_2SiH)_6$ In this compound one has not only six silicon atoms, but more particularly six reactive functional groups which can lead not only to other reactive monomers but also to reactive polymers having a high concentration of fluorines.

There is also reported at this time a series of highly halogenated phosphorus compounds. Here the interest is to prepare reactive monomers containing polyhalogen substituents, as well as the phosphorus-oxygen grouping which some early studies reported from here indicated would increase thermal stability. Among the compounds reported are: $(C_6F_5)_2PC_6H_5$

and $(C_6Cl_5)_2PC_6H_5$ as well as their oxides:

$$(C_6F_5)_2P(O)C_6H_5 \text{ and } (C_6Cl_5)_2P(O)C_6H_5$$

The important functional groups can be introduced by either of the two following syntheses:

$$\begin{tikzcd} \underline{p}\text{-}Me_3SiC_6Cl_4M + C_6H_5PCl_2 \arrow[dr] & \\ & (\underline{p}\text{-}Me_3SiC_6Cl_4)_2PC_6H_5 \\ Me_3SiCl + (\underline{p}\text{-}MC_6Cl_4)_2PC_6H_5 \arrow[ur] & \end{tikzcd}$$

The routes to $\underline{p}$-$Me_3SiC_6F_4M$ and $\underline{p}$-$HMe_2SiC_6F_4M$ are unlike those to the formally analogous $\underline{p}$-$Me_3SiC_6Cl_4M$ and $\underline{p}$-$HMe_2SiC_6Cl_4M$.

In this connection mention should be made of some "mixed" polyhalogen types. We have shown in some recent studies that it is possible to form a mono-Grignard reagent with ease from pentachloropyridine. The halogen involved predominantly in this reaction is in the 4-position, leading to 2,3,5,6-tetrachloro-4-pyridylmagnesium chloride. From this there is readily prepared the important 2,3,5,6-tetrachloro-4-(hydrodimethylsilyl)pyridine:

$$C_5Cl_5N + Mg \longrightarrow 4\text{-}ClMgC_5Cl_4N$$

$$4\text{-}ClMgC_5Cl_4N + HMe_2SiCl \longrightarrow 4\text{-}HMe_2SiC_5Cl_4N$$

The relatively high reactivity of the nuclear halogens should provide a direct route to a reactive polyfunctional monomer having both fluorine and chlorine atoms:

$$HMe_2SiC_5Cl_3N\text{-}(CF_2)_n\text{-}NC_5Cl_3SiMe_2H$$

The pyridine nucleus also contributes to thermal stability.

II. THE PREPARATION AND SOME REACTIONS OF TRIPHENYLSILYLSODIUM AND METHYLDIPHENYLSILYLSODIUM[1]

A. INTRODUCTION

The preparation of silylmetallic species by the cleavage of polysilanes with alkali metals in ethereal solvents, generally THF, is well established and has been reviewed.[2,3] However, this work emphasized the fact that whereas lithium, potassium, rubidium and cesium derivatives are relatively easily obtained, the corresponding silylsodium compounds are almost completely unknown.

Triphenylsilylsodium has been prepared by the cleavage of hexaphenyldisilane in 1,2-dimethoxyethane[4] or in liquid ammonia.[5] However, in the ethereal solvent this compound is difficult to prepare and unstable, whereas preparations in liquid ammonia are complicated by the presence of the highly reactive solvent.

It was reported by Coates and co-workers[6] that solutions of triphenylstannylsodium could be prepared by the action of sodium naphthalenide on hexaphenyldistannane, tetraphenylstannane, or bromotriphenylstannane. In an extension of this work it was shown[7] that triphenylsilylsodium can be prepared in THF by the action of sodium naphthalenide on triphenylsilane, hexaphenyldisilane, or chlorotriphenylsilane. However, in all these reactions the stoichiometric quantity of sodium naphthalenide calculated to convert the tin or silicon compounds to the corresponding sodium derivatives was employed.

In an excellent investigation, Eisch[8] has shown that solutions of the lithium-biphenyl complexes in THF are remarkably effective in promoting certain reactions which proceed only slowly, or not at all, with the bulk metal. In this investigation it was shown that catalytic quantities of biphenyl in the presence of the bulk metal was frequently effective.

We have found[1] that triphenylsilylsodium, or methyldiphenylsilylsodium, can be easily prepared in THF from the corresponding disilanes, using metallic sodium in the presence of small quantities of naphthalene or biphenyl, or from the corresponding chlorosilanes and sodium in the presence of naphthalene. However all attempts to prepare dimethylphenylsilylsodium by the cleavage of 1,1,2,2-tetramethyl-1,2-diphenyldisilane under similar conditions failed.

Some of the properties of the above silylsodium compounds have been examined and have been found to be different to those of the analogous silyllithium compounds.

B. RESULTS

The reaction between hexaphenyl-, or dimethyltetraphenyldisilane (x moles) and excess sodium in the presence of naphthalene or biphenyl (0.1-0.2 x moles) in THF gave solutions of triphenylsilyl- and methyldiphenyl silylsodium during 5-12 hours. The presence of the silylmetallic species in these solutions was demonstrated by: (a) hydrolysis to the known silanes; and (b) reaction with a suitable chlorosilane to give the known disilanes (see Table I). The yields of derivatized products obtained from these reactions were comparable to those obtained from the known silyllithium compounds,[2] indicating that the silylsodium compounds must have originally been present in good yield. However, it was not possible to estimate the concentration of the silylmetallic species directly by the established double titration technique[9] for, on completion of the reaction, excess sodium naphthalenide or biphenylide, was always present. In an attempt to overcome this difficulty, the solutions were decanted from the excess sodium and treated with a further amount of the respective disilane. It was observed that the greenish brown solutions acquired the red-brown color characteristic of silylmetallic compounds,[2] during 30 mins. to 1 hour. Working on the assumption that all of the anion radical had been consumed, the solutions were then analyzed by double titration with allyl bromide.[9] In this way it was estimated that triphenylsilylsodium was obtained in ca. 80% yield from hexaphenyldisilane and sodium in the presence of biphenyl, while methyldiphenylsilylsodium was obtained in ca. 75% yield from dimethyltetraphenyldisilane under comparable conditions.

It was noted that the cleavage reaction proceeded more rapidly in the present of biphenyl than with comparable molar amounts of naphthalene. For instance hexaphenyldisilane (0.05 mole) was cleaved by sodium in the presence of biphenyl (0.01 mole) during ca. 5 hours, whereas a similar reaction with naphthalene required ca. 12 hours.

Having established that the silylsodium compounds could be obtained from their disilanes it was logical to attempt their preparation from the corresponding chloro-

Table I

Products Obtained from Reactions of Triphenylsilylsodium and Methyldiphenylsilylsodium

Silylsodium Compound	Reactant	Products %	Products from Silyllithium[c] %
Ph_3SiNa	H_3O^+	Ph_3SiH 83[a] (67)[b]	Ph_3SiH 81
$MePh_2SiNa$	H_3O^+	$MePh_2SiH$ 71[a] (66.7)[b]	$MePh_2SiH$ 79
Ph_3SiNa	Me_3SiCl	$Me_3SiSiPh_3$ 78.5[a] (70)[b]	$Me_3SiSiPh_3$ 79[2]
$MePh_2SiNa$	Ph_3SiCl	$MePh_2SiSiPh_3$ 67[a]	$MePh_2SiSiPh_3$ 58[2]
Ph_3SiNa	PhCl	Ph_6Si_2 19[a], Ph_4Si 45	Ph_6Si_2 66.3, Ph_4Si 17.7[2]
$MePh_2SiNa$	PhCl	$MeSiPh_3$ 61[a], $MePh_2SiSiPh_2Me$ 16.7	$MePh_2SiSiPh_2Me$ 57, $MeSiPh_3$ 16.8
Ph_3SiNa	*n*-BuBr	Ph_3SiBu[a]-*n* 22 Ph_6Si_2 43	Ph_3SiBu-*n* 10 Ph_6Si_2 60[2]
Ph_3SiNa	$HSiCl_3$	Ph_6Si_2[a] 13.3 $(Ph_3Si)_3SiH$ 17	Ph_6Si_2 20.6 Ph_3SiH 29.5 $(Ph_3Si)_3SiH$ 4.4[2]

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a. Silylsodium compounds prepared from disilane
b. Silylsodium compounds prepared from chlorosilane
c. Silyllithium compounds prepared from disilane

silanes. Here difficulty was experienced, for although the reaction between chlorotriphenylsilane or chlorodiphenylmethylsilane and sodium proceeded smoothly in the presence of naphthalene to give the required silylsodium compounds, a similar reaction did not occur in the presence of biphenyl. In the latter cases, the characteristic blue-green color of the sodium biphenylide initially formed on the surface of the sodium, but was rapidly discharged and did not reform. Examination of the reaction mixtures by v.p.c. at this stage showed that biphenyl was still present.

Slightly lower yields of derivatized products were obtained when the silylsodium compounds were prepared from the chlorosilanes than when they were prepared from the disilanes. However, it has been reported that lower yields of silyllithium compounds result from the action of lithium on chlorosilanes than from the corresponding disilanes.[2] Attempts to prepare dimethylphenylsilylsodium by the cleavage of 1,1,2,2-tetramethyl-1,2-diphenyldisilane with sodium in the presence of naphthalene or biphenyl failed. Initially the green, or blue-green, color of the anion radical was formed, but this was replaced during 6-8 hours by a red-brown color. Examination of hydrolyzed aliquots of the reaction mixtures at this stage showed the hydrocarbons had been consumed and much unreacted disilane remained, only traces of dimethylphenylsilane could be detected in either case. A small amount of 4,4'-bis(dimethylphenylsilyl)-biphenyl (2%) was isolated from the biphenyl reaction.

In order to attempt to establish the mode of destruction of the aromatic hydrocarbons, the reactions of 1,1,2,2-tetramethyl-1,2-diphenyldisilane (x moles) with sodium in the presence of naphthalene or biphenyl (x moles) were examined. Under these conditions all of the disilane was consumed in the biphenyl reaction and nearly all in the naphthalene reaction during 24 hours. Some unreacted hydrocarbon remained in both reaction mixtures.

After hydrolysis, v.p.c. indicated that both reaction mixtures were complex, but it was possible to isolate some unreacted hydrocarbon from both reactions. The biphenyl reaction also yielded 19% of 4,4'-bis(dimethylphenylsilyl)-biphenyl, whereas 3.5% of 1-dimethylphenylsilylnaphthalene was isolated from the naphthalene reaction.

In an attempt to discover if 4,4'-bis(dimethylphenylsilyl)biphenyl was formed by the attack of an intermediate silylmetallic compound on biphenyl the reaction of methyldiphenylsilyllithium with this compound was investigated.

After 12 hours, 7.1% of 4,4′-bis(dimethylphenylsilyl)biphenyl was isolated subsequent to hydrolysis. Dimethylphenylsilane was identified among the products by v.p.c. but was not isolated.

The stability of solutions of triphenylsilyl and methyldiphenylsilylsodium was determined by periodically estimating the concentration of silylmetallic species by double-titration with allyl bromide.[9] The excess anion radical had previously been removed from these solutions by treatment with additional amounts of the appropriate disilane. No change in the concentration of an 0.47 molar solution of triphenylsilylsodium could be detected during 50 hours. In the same time the concentration of an 0.45 molar solution of methyldiphenylsilylsodium dropped to 0.41 molar.

A limited number of reactions of triphenylsilylsodium and methyldiphenylsilylsodium with halogen compounds were investigated; the products obtained are reported in Table I. In all cases considerable difference in product ratio was observed between reactions of the silylsodium compounds and comparable reactions of their silyllithium analogs.

C. DISCUSSION

The reaction of sodium with naphthalene or biphenyl in THF gives rise to the highly reactive naphthalenide or biphenylide anion radicals, by transfer of an electron from the metal into the lowest empty molecular orbital of the aromatic hydrocarbon (Ar):[10,11]

$$\mathrm{Ar} + \mathrm{Na} \overset{\mathrm{THF}}{\rightleftarrows} \mathrm{Ar}^{\dot{-}}\mathrm{Na}^{+}$$

Such anion radicals are capable of transferring the extra electron to a suitable acceptor molecule of higher electron affinity, during which process the hydrocarbon is regenerated.[11] It has been shown[7] that this type of electron transfer probably occurs between equimolar amounts of sodium naphthalenide and a triphenylhalosilane to give, initially, a triphenylsilyl radical. A reaction of this type could simply account for the formation of the silylsodium compounds obtained in this work.

This type of reaction between an aryl substituted disilane or chlorosilane[12] and an anion radical can be depicted as follows:

$$\mathrm{R_3SiSiR_3} + \mathrm{Ar}^{\dot{-}}\mathrm{Na}^{+} \longrightarrow \mathrm{R_3Si}\cdot + \mathrm{R_3SiNa} + \mathrm{Ar} \tag{1}$$

$$\mathrm{R_3SiCl} + \mathrm{Ar}^{\dot{-}}\mathrm{Na}^{+} \longrightarrow \mathrm{R_3Si}\cdot + \mathrm{NaCl} + \mathrm{Ar} \tag{2}$$

In either reaction an intermediate silyl radical would be formed, but this would be expected to be rapidly transformed to a silylsodium compound by reaction with either a further anion radical, or metallic sodium:

$$R_3Si\cdot + Ar^{\overline{\cdot}}Na^{+} \longrightarrow R_3SiNa + Ar$$

$$R_3Si\cdot + Na \longrightarrow R_3SiNa$$

In the case of the chlorosilane reactions, the silylsodium compound initially formed would be expected to immediately couple with unreacted silyl halide to form a disilane, which, in turn, would be cleaved to the silylsodium compound. During the reaction of chlorotriphenylsilane with sodium in the presence of naphthalene this initial coupling was in fact observed and hexaphenyldisilane was isolated as an intermediate product.

As only a small amount of aromatic hydrocarbon was required to convert a relatively large amount of the disilane, or chlorosilane, to the corresponding silylsodium compound, it must be assumed that the hydrocarbon liberated in reactions (1) or (2) was immediately converted back to the anion radical, by reaction with the excess sodium, to repeat the cycle.

A similar type of electron transfer mechanism to that described above was suggested by Eisch[8] to explain the high yields of, for instance, phenol obtained, subsequent to hydrolysis, by treatment of anisole with the 2:1 lithium-biphenyl adduct.

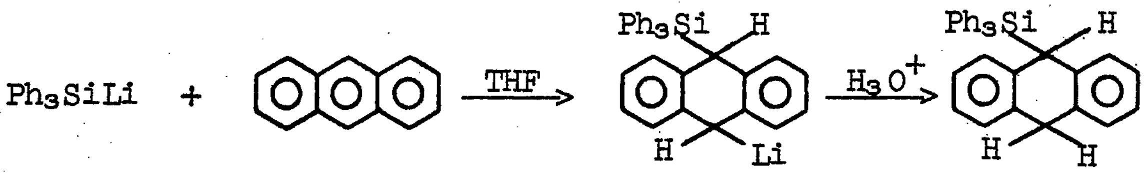
It has been shown that the rate of electron transfer between an aromatic hydrocarbon anion radical and a suitable acceptor molecule is dependent on the difference in electron affinity between the parent hydrocarbon and acceptor molecule.[11] Naphthalene has a higher electron affinity than biphenyl; thus, assuming that similar factors govern the rate of electron transfer between sodium naphthalenide, or biphenylide, and hexaphenyl- or 1,2-dimethyltetraphenyldisilane, it is apparent why biphenyl promotes more rapid cleavage of the disilane than naphthalene.

One fact which is difficult to explain is why triphenylsilyl- and methyldiphenylsilylsodium are readily prepared from the corresponding chlorosilanes and sodium in the presence of naphthalene, but not in the presence of biphenyl. It was certainly not because the hydrocarbon was consumed by any side reactions as v.p.c. showed that a considerable amount of biphenyl remained even after reaction had ceased.

As previously stated, reaction of sodium naphthalenide, or biphenylide, with a disilane apparently splits the silicon-silicon bond to give an anionic fragment and, presumably, a radical fragment, (Equations (1) and (2)). In the case of hexaphenyldisilane or 1,2-dimethyltetraphenyldisilane, neither of the fragments formed apparently attacked the hydrocarbons to any great extent. However, in the case of 1,1,2,2-tetramethyl-1,2-diphenyldisilane, evidence suggests that one, or both, of the fragments reacted fairly rapidly with either naphthalene or biphenyl to give, in addition to other products, 1-dimethylphenylsilylnaphthalene and 4,4′-bis(dimethylphenylsilyl)biphenyl, respectively.

Currently, sufficient evidence is not available to decide exactly how the above compounds arose, but it is interesting to note that dimethylphenylsilyllithium reacts with biphenyl to give, subsequent to hydrolysis, some 4,4′-bis(dimethylphenylsilyl)biphenyl.

Reactions of silyllithium compounds with aromatic hydrocarbons have been previously reported.[2] For instance triphenylsilyllithium[13] reacts with anthracene to give, subsequent to hydrolysis, 9-triphenylsilyl-9,10-dihydroanthracene. It is possible that a reaction of the above



type could account for the formation of the 4,4′-bis(dimethylphenylsilyl)biphenyl obtained in this work, if a dihydro compound formed on hydrolysis was relatively unstable and underwent dehydrogenation during work-up.

<u>The reactions of triphenylsilyl and methyldiphenylsilylsodium.</u>

The technique used to determine the actual concentrations of the silylsodium compounds is somewhat open to question, for it is by no means certain that addition of excess disilane to a solution of a silylsodium compound and anion radical resulted in complete consumption of the anion radical. Nevertheless the concentrations of the silylsodium solutions, as determined by this method, are in fair agreement with the yields of derivatized products obtained on treatment with acid or a suitable chlorosilane.

The stability of the silylsodium compounds in THF appears to approach that of the corresponding silyllithium compounds,[14] a fact which is perhaps rather surprising as it is known that alkyl and arylsodium compounds are in general much less stable in ethereal solvents than the comparable lithium compounds.[10]

The most significant difference in reactivity between the silylsodium and silyllithium compounds so far observed is shown by their reactions with halogen compounds, in particular with chlorobenzene. The reaction of a silylmetallic compound with an organic halide can proceed by at least two routes:[2] (a) nucleophilic attack of the silylmetallic on the halogen compound to give a tetrasubstituted silane and a metallic halide:

$$R_3SiM + R'X \longrightarrow R_3SiR' + MX$$

(b) by an exchange reaction resulting in the formation of a silylhalide and a new organometallic compound:

$$R_3SiM + R'X \longrightarrow R_3SiCl + R'M$$

This reaction frequently leads to the formation of high yields of disilanes by coupling of the chlorosilane with unreacted silylmetallic compound:

$$R_3SiM + R_3SiCl \longrightarrow R_3SiSiR_3 + MCl$$

The isolation of 45% of tetraphenylsilane from the reaction of triphenylsilylsodium with chlorobenzene, compared with the 17% isolated from a similar reaction of triphenylsilyllithium,[2] is typical of the increased yields of coupled products obtained from the reactions of the silylsodium compounds with halogen compounds (See Table I). The increased yields of coupled products suggest that the silylsodium compounds prepared in this work are more powerful nucleophilic reagents than the corresponding silyllithium compounds, which might be expected if a silicon-sodium bond is more ionic than a comparable silicon-lithium bond.

The reaction of triphenylsilylpotassium in ether with chlorobenzene has been investigated.[2] In this case the yield of tetraphenylsilane (53%) was greater than the yields isolated from the reactions with either triphenylsilylsodium or lithium in THF. However, the difference in yields may have been due, in part, to the difference in solvent, so no direct comparison can be made.

The yield of tris(triphenylsilyl)silane (17%) obtained from triphenylsilylsodium and trichlorosilane is considerably greater than that obtained using triphenylsilyllithium (4.4%).[2] This fact is of considerable significance for it indicates that steric factors alone were not entirely responsible for the low yield of this silane obtained from triphenylsilyllithium and trichlorosilane.

D. EXPERIMENTAL

All reactions were carried out in oven-dried glassware, under an atmosphere of dry, oxygen free, nitrogen.

THF was purified by distillation from sodium benzophenone ketyl after initial drying over sodium.

The disilanes were all prepared and purified by standard procedures.[3]

Organosilicon halides were obtained from Dow Corning Corp. and were used without further purification. Chlorobenzene and n-butyl bromide, Eastman Kodak White Label, were dried over phosphorous pentoxide before use.

Chromatography was carried out over Woelm neutral alumina. Unless otherwise stated all solid compounds were identified by mixed melting points, and comparison of their infrared spectra with authentic materials. Liquids, or low melting solids, were identified by comparison of their boiling points, v.p.c. retention times and infrared spectra with authentic materials. The physical properties of these materials can be found in references 15 and 16.

Infrared spectra were determined using a Perkin Elmer, Model 21 Spectrophotometer.

V.p.c. analyses were carried out with an F and M Model 500 gas chromatograph using an 18 x 1/4 in. column packed with silicon gum rubber, S.E. 30, on Chromosorb W (1:20).

Melting points were determined using a Mel Temp apparatus and are uncorrected.

Triphenylsilylsodium by cleavage of hexaphenyldisilane with sodium in the presence of (1) biphenyl and (2) naphthalene

(1) Hexaphenyldisilane (13 g, 0.025 mole) and biphenyl (0.75 g, 0.005 mole) were placed in a nitrogen flushed three-necked flask fitted with a teflon paddle stirrer. THF (100 ml) was added, then sodium (2.3 g, 0.1 g atom) was cut into the mixture through an emergent nitrogen stream. The sodium

immediately turned blue-green on the cut surfaces and after stirring for 5 min. the whole solution turned the same color. When stirring was briefly interrupted unreacted hexaphenyldisilane settled to the bottom of the flask. After 5 hours stirring no unreacted disilane remained. The green solution was decanted through a short tube plugged with glass wool into a nitrogen flushed dropping funnel, before being added dropwise with stirring to 20% hydrochloric acid (100 ml). The green color was discharged through a transient red-brown and heat was evolved. The ethereal layer was separated, dried over anhydrous magnesium sulphate, concentrated and the residue distilled under reduced pressure to give triphenylsilane b.p. 135°C/0.1 mm, m.p. 43-46°C (10.8 g, 83%).

(2) A similar reaction was carried out using 0.65 g (0.005 mole) of naphthalene. The solution turned dark green on stirring and twelve hours of stirring was required to consume all the disilane. The mixture was hydrolyzed and worked up as described above to give triphenylsilane (10 g, 77%).

Preparation of methyldiphenylsilylsodium by the cleavage of 1,2-dimethyltetraphenyldisilane with sodium in the presence of biphenyl.

The reaction between 1,2-dimethyltetraphenyldisilane (9.85 g, 0.025 mole), sodium (2.3 g, 0.1 g. atom) and biphenyl (0.75 g, 0.005 mole) in THF (100 ml) was carried out in a similar manner to the hexaphenyldisilane reaction; the reaction mixture again turned blue-green. After stirring 6 hours the solution was hydrolyzed and worked up in a similar manner to the hexaphenyldisilane reaction to give methyldiphenylsilane, b.p. 84.5-86°C/0.3 mm (7.05 g, 71%).

Attempted preparation of triphenylsilylsodium and methyldiphenylsilylsodium by reaction of the corresponding chlorosilanes with sodium in the presence of biphenyl.

Chlorotriphenylsilane (14.5 g, 0.05 mole) and biphenyl (1.5 g, 0.01 mole) were dissolved in THF (100 ml). Sodium (4.6 g, 0.2 g. atom) was added in small pieces through an emergent stream of nitrogen and immediately turned blue-green on the cut surfaces. The mixture was stirred and the blue-green color was rapidly discharged, the sodium acquiring a tarnished appearance. Examination of the reaction mixture by v.p.c. after 5 hours showed the presence of unreacted biphenyl.

A similar reaction with methyldiphenylchlorosilane gave identical results, a considerable quantity of unreacted biphenyl again being detected by v.p.c. after 5 hours.

<u>Preparation of triphenylsilylsodium and methyldiphenylsilylsodium by the reaction of the corresponding chlorosilanes with sodium in the presence of naphthalene</u>.

Chlorotriphenylsilane (14.5 g, 0.05 mole) and naphthalene (1.28 g, 0.01 mole) were dissolved in THF and sodium (4.6 g, 0.2 g. atom) was added. A faint green color was formed on the surface of the sodium which was not completely discharged on commencement of stirring. After 15 min a white solid began to separate out of solution; a portion of this was removed after 1 hour and was shown to be almost pure hexaphenyldisilane. After 2 hours stirring the solution turned deep green. The reaction was stirred for a total of 5 hours before the deep green solution was decanted from the excess sodium, hydrolyzed with acid, and worked up as previously described to give triphenylsilane (8.7 g, 67%).

A similar reaction with methyldiphenylchlorosilane (11.6 g, 0.05 mole) gave methyldiphenylsilane (6.6 g, 66%).

<u>Reaction of triphenylsilylsodium and chlorotrimethylsilane</u>.

A solution of triphenylsilylsodium prepared from hexaphenyldisilane (13 g, 0.025 mole), biphenyl (0.75 g, 0.005 mole) and sodium (2.3 g, 0.1 g. atom) in THF (100 ml), was added dropwise with stirring to chlorotrimethylsilane (10.85 g, 0.1 mole) in THF (50 ml). The blue-green solution was immediately decolorized through a transient red-brown with evolution of heat. The reaction mixture was hydrolyzed with dilute hydrochloric acid, the ethereal layer separated, dried over magnesium sulphate, concentrated and the residue recrystallized twice from ethanol to give 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 104-105°C (13.0 g, 78.5%).

A similar reaction using triphenylsilylsodium prepared from chlorotriphenylsilane (14.5 g, 0.05 mole) gave 11.6 g (70%) of the above compound.

<u>Reaction of methyldiphenylsilylsodium with chlorotriphenylsilane</u>.

A solution of methyldiphenylsilylsodium, prepared from 1,2-dimethyltetraphenyldisilane (9.85 g, 0.025 mole) biphenyl (0.75 g, 0.005 mole), and sodium (2.3 g, 0.1 g. atom) in THF (100 ml) was added to a solution of chlorotriphenylsilane

(14.5 g, 0.05 mole) in THF (50 ml). The blue-green solution was immediately decolorized through a transient red-brown with slight evolution of heat. The reaction mixture was hydrolyzed with dilute hydrochloric acid, the ethereal layer separated, dried over magnesium sulphate and concentrated. The residue was dissolved in the minimum quantity of benzene and chromatographed over alumina. Elution with petroleum ether gave methylpentaphenyldisilane, m.p. 146-7°C (15.5 g, 56%).

Determination of the stabilities of triphenylsilylsodium and methyldiphenylsilylsodium in THF.

The silylsodium compounds were prepared from 0.025 mole of the corresponding disilanes, 0.005 mole of biphenyl and 0.1 g atom of sodium in 150 ml of THF. The dark blue-green solutions were decanted away from the excess sodium and treated with a further 0.005 mole of the corresponding disilanes. The blue-green colors faded during 30-60 min being replaced by red-brown colors. The solutions were stored under nitrogen and periodically analyzed by double titration with allyl bromide.[9] No change was observed in the concentration of triphenylsilylsodium, initially 0.047 molar, during 100 hours. During the same time the concentration of methyldiphenylsilylsodium, initially 0.045 molar, dropped to 0.041 molar.

Reaction of triphenylsilylsodium and chlorobenzene.

A solution of triphenylsilylsodium, prepared from hexaphenyldisilane (0.025 mole) was added dropwise with stirring to chlorobenzene (12.5 g, 0.1 mole) in THF (50 ml) during 30 mins. The green solution turned dark yellow and some solid was precipitated. Color Test I[17] was negative after the addition. The mixture was hydrolyzed with dilute hydrochloric acid and filtered giving a solid m.p. 237-293°C (7.5 g) which on extraction with hot benzene left hexaphenyldisilane (2.5 g, 19%). The ethereal layer was separated, dried over magnesium sulphate, combined with the benzene extracts of hexaphenyldisilane and concentrated. Recrystallization of the residue from ethyl acetate gave tetraphenylsilane, m.p. 233-235°C (7.55 g, 45%).

Reactions of methyldiphenylsilylsodium and methyldiphenylsilyllithium with chlorobenzene.

A solution of methyldiphenylsilylsodium, prepared from 1,2-dimethyltetraphenyldisilane (9.85 g, 0.025 mole) was added dropwise with stirring to a solution of chlorobenzene (12.5 g, 0.1 mole) in THF (50 ml) during 30 mins. The deep blue-green color changed to orange-yellow and Color Test I was negative. The reaction mixture was hydrolyzed with dilute hydrochloric acid, and the ethereal layer was dried and distilled under reduced pressure to give methyltriphenylsilane, b.p. 141-143°C/0.02 mm (7.5 g, 61%). Recrystallization of the stillpot residue from petrol ether (b.p. 70-80°) gave 1,2-dimethyltetraphenyldisilane (1.65 g, 16.7%).

A similar reaction was carried out with methyldiphenylsilyllithium, prepared by the reported procedure.[2] Identical work-up gave 16.8% of methyltriphenylsilane and 57.9% of 1,2-dimethyltetraphenyldisilane.

Reaction of triphenylsilylsodium with n-butyl bromide.

A solution of triphenylsilylsodium, prepared from 13 g (0.025 mole) of hexaphenyldisilane, was added to a solution of *n*-butyl bromide (13.7 g, 0.1 mole) in THF (50 ml). The blue-green solution was immediately decolorized with evolution of heat, and some solid precipitated. The reaction mixture was hydrolyzed with dilute hydrochloric acid and filtered; the residue was hexaphenyldisilane (5.6 g, 43%). The ethereal layer was dried and concentrated to give an oil which was dissolved in the minimum amount of benzene and chromatographed over alumina. Elution with petrol ether (b.p. 60-70°) gave an oily solid which was crystallized from methanol to give *n*-butyltriphenylsilane, m.p. 90-91° (3.5 g, 22%).

Reaction of triphenylsilylsodium with trichlorosilane.

Triphenylsilylsodium was prepared from hexaphenyldisilane (25.9 g, 0.05 mole). After removal of the excess anion radical by addition of further hexaphenyldisilane (5.0 g), analysis by double titration[9] indicated the presence of 0.0875 mole of the silylmetallic compound. The deep green solution was added dropwise with stirring to a solution of trichlorosilane (4 g, 0.029 mole) in ether (50 ml) at -60°C. After 3 hours stirring Color Test I was negative. The solution was allowed to warm to room temperature, hydrolyzed with dilute hydrochloric acid and filtered to give hexaphenyldisilane (4.1 g, 13.3%). Concentration of the dried ethereal layer gave a yellow oil which was chromatographed over alumina. Elution with petroleum ether (b.p. 60-70°C) gave an oil which was not identified. Elution with carbon tetrachloride gave a gummy solid, which was recrystallized from a mixture of ethylacetate and methanol (10:90) to give tris(triphenylsilyl)silane, m.p. 205-207°C (3.95 g, 17%).

Attempted preparation of dimethylphenylsilylsodium by reaction of sodium with 1,1,2,2-tetramethyl-1,2-diphenyldisilane in the presence of (1) biphenyl and (2) naphthalene.

(1) 1,1,2,2-Tetramethyl-1,2-diphenyldisilane (13.5 g, 0.05 mole) and biphenyl (1.5 g, 0.01 mole) were dissolved in THF (100 ml). Sodium (4.6 g, 0.2 g. atom) was cut into the reaction flask and stirring was commenced. After 15 mins the solution turned dark blue, a color which changed to light brown after 6 hours. A portion of the mixture was hydrolyzed and examined by v.p.c.; only a small amount of dimethylphenylsilane and much 1,1,2,2-tetramethyldiphenyldisilane could be detected. The solution was decanted from excess sodium and hydrolyzed with dilute acid. Concentration of the dried ethereal layer gave an oil which was distilled under reduced pressure to give 1,1,2,2-tetramethyldiphenylsilane, b.p. 108.5-110°C/0.3 mm, (6.2 g, 46%). The stillpot residue was recrystallized from methanol to give 4,4'-bis-(dimethylphenylsilyl)biphenyl, m.p. 74-75°C, (0.08 g, 2%).

(2) A similar reaction was carried out in the presence of naphthalene (1.28 g, 0.01 mole). On addition of sodium and stirring the solution immediately turned dark green, but this color changed to red-brown after 8 hours. Examination of a hydrolyzed sample by v.p.c. showed the presence of at least 4 volatile components, but only a trace of dimethylphenylsilane and unreacted 1,1,2,2-tetramethyldiphenyldisilane could be identified. Work-up as described above gave 1,1,2,2-tetramethyldiphenyldisilane (5.2 g, 38.5%). No further products could be isolated.

Reaction of 1,1,2,2-tetramethyldiphenyldisilane (x moles) with (1) biphenyl (2x moles), (2) naphthalene (x moles), and sodium in THF.

1,1,2,2-Dimethyltetraphenyldisilane (6.75 g, 0.025 mole) and biphenyl (7.6 g, 0.05 mole) were dissolved in THF (75 ml). Sodium (2.3 g, 0.1 g. atom) was added and stirring commenced. The solution turned deep blue. After 24 hours a portion of the reaction mixture was hydrolyzed and examined by v.p.c., no unreacted disilane could be detected. The reaction mixture was decanted from excess sodium and hydrolyzed by addition to dilute acid. Concentration of the dried ethereal layer gave an oil which was sublimed (100°C/5 mm) to give biphenyl (3.0 g, 39.5%). Crystallization of the residue from methanol gave 4,4'-bis(dimethylphenylsilyl)biphenyl (2 g, 19%).

(2) A similar reaction was carried out between 1,1,2,2-tetramethyldiphenylsilane, (40 g, 0.15 mole), naphthalene (19.2 g, 0.15 mole) and sodium (9.2 g, 0.4 g. atom) in THF (250 ml). After 24 hours v.p.c. indicated that the disilane had been consumed. Concentration of the dried ethereal layer, subsequent to hydrolysis, gave a liquid which was sublimed (110°C/7 mm) to give naphthalene (3.0 g, 15.7%). The sublimation residue was distilled through a 18 in. x 6 mm Nester Faust spinning band column to give 1-dimethylphenylsilylnaphthalene, b.p. 124°C/0.04 mm, m.p. 53-54°C (1.7 g, 3.5%). Numerous other products were present as evidenced by v.p.c., but none has been isolated in a pure state.

1-Dimethylphenylsilylnaphthalene was prepared as a reference compound from 1-lithionaphthalene[18] (0.1 mole) and dimethylphenylchlorosilane (0.1 mole) in ether at 0 ± 5° during 24 hours. Hydrolysis and distillation gave 65% of the required product, b.p. 136-138.5°C/1.5 mm. $C_{18}H_{18}Si$ requires Si, 10.67%. Found, Si, 10.56, 10.62.

Reaction of dimethylphenylsilyllithium with biphenyl.

Dimethylphenylsilyllithium[2] (0.1 mole) in THF (100 ml) was added to biphenyl (15.4 g, 0.1 mole) in THF (50 ml). The reaction mixture was stirred 48 hours, hydrolyzed with dilute hydrochloric acid, and the dried ethereal extracts concentrated. The residue was sublimed (100°C/5 mm) to give biphenyl (6.1 g, 39.5%) after crystallization from ethanol. Repeated crystallization of the sublimation residue from methanol gave 4,4'-bis(dimethylphenylsilyl)biphenyl (1.5 g, 7.1%).

III. SYNTHESES OF SOME PENTAHALOPHENYL-SUBSTITUTED SILANES

A. INTRODUCTION

The ultraviolet data for a number of pentachlorophenyl- and pentafluorophenyl-substituted silanes were recorded and published earlier.[19] All the pentachlorophenyl compounds were prepared in moderate yields by the coupling of pentachlorophenylmagnesium chloride[20] with the appropriate chloro- or dichloropermethylated silane in tetrahydrofuran: the pentafluorophenyl compounds were prepared similarly *via* pentafluorophenyllithium.[21]

$$2\ C_6Cl_5MgCl + Cl(SiMe_2)_nCl \longrightarrow C_6Cl_5(SiMe_2)_nC_6Cl_5$$

It was convenient to use the Grignard reagent for the majority of these preparations, and no examination of similar reactions with the lithium reagents was made. Experiments carried out in related work indicate that the use of pentachlorophenyllithium would have been entirely satisfactory. The lithium reagent, chosen for the preparation of the pentafluorophenyl compounds, returned a high yield of product.

Although pentafluorophenyl-silicon compounds are comparatively well-known,[22] the only pentachlorophenylsilicon compound previously reported was pentachlorophenyltrichlorosilane, formed in low yield by the chlorination of phenyltrichlorosilane.[23]

Attempts to prepare some of the perphenylated analogs failed, such failure probably due to steric factors. No products were obtained from reactions of pentachlorophenylmagnesium chloride with 1,4-dichlorooctaphenyltetrasilane and 1,5-dichlorodecaphenylpentasilane; of pentachlorophenyllithium with 1,4-dichlorooctaphenyltetrasilane, 1,4-dibromooctaphenyltetrasilane, and 1,2-dibromotetraphenyl disilane; or of pentafluorophenyllithium with 1,4-dichlorooctaphenyltetrasilane. At the temperatures employed, no reaction was found to occur in any case.

Coupling between pentachlorophenylmagnesium chloride and 1-hydro-3-chlorohexamethyltrisilane in tetrahydrofuran was attempted in an effort to prepare 1-hydro-(3-pentachlorophenyl)hexamethyltrisilane. No tractable products resulted from the reaction. Similar failure resulted from the use of the Grignard reagent in diethyl ether,[24] and the lithium compound in tetrahydrofuran.

Several attempts were made to produce, from hexachlorobenzene, a perchlorinated reactive species containing the active constituents in the 1,4- position. Preparations of the pentachlorophenylmagnesium chloride in the usual manner result in the formation of a small amount (*ca.* 5%) of tetrachlorobenzene on hydrolysis, indicating the presence of the 1,4-di-Grignard reagent.[20] However, efforts to raise this proportion of the di-Grignard reagent, either by the use of di-*n*-butyl ether as solvent or by means of an exchange reaction between benzylmagnesium chloride and hexachlorobenzene,[20] were unsuccessful. 1,2,4,5-Tetrachlorobenzene was metalated by *n*-butyllithium but no tractable products resulted on derivatization with chlorotrimethylsilane.

Physical Properties

As expected, all the pentachlorophenyl derivatives prepared were white, crystalline solids with fairly sharp melting points, whereas the two bis(pentafluorophenyl) derivatives of the mono- and trisilanes were high-boiling liquids. Table II lists the melting points of the pentachlorophenyl compounds. The bis(pentafluorophenyl)dimethylsilane and 1,3-bis(pentafluorophenyl)hexamethyltrisilane had boiling points of 138-140°C/14 mm and 116°C/0.07 mm, respectively.

Table II

The melting points of some pentachlorophenyl-substituted silanes

Compound	M.P. °C
$C_6Cl_5SiMe_3$	116-117
$C_6Cl_5SiMe_2C_6Cl_5$	232-234
$C_6Cl_5(SiMe_2)_2C_6Cl_5$	223-224
$C_6Cl_5(SiMe_2)_3C_6Cl_5$	165-166
$C_6Cl_5(SiMe_2)_4C_6Cl_5$	143-145
$C_6Cl_5(SiMe_2)_5C_6Cl_5$	129-130
$C_6Cl_5(SiMe_2)_6C_6Cl_5$	148-149
$C_6Cl_5(SiMe\cdot Ph)C_6Cl_5$	164-165

Spectral Properties

(a) Infrared spectra

The infrared spectra of all the pentachlorophenyl compounds showed a strong absorption at ca. 9.2 μ, doubtless arising from a Si-C_6Cl_5 vibration, and a strong singlet at ca. 11.5 μ which also appeared to be characteristic of a C_6Cl_5 grouping. Other bands appearing in the spectrum were consistent with the relevant substituted permethylated silane. Spectra were determined using a Perkin-Elmer Model 21 spectrophotometer, with carbon tetrachloride as solvent.

(b) Ultraviolet spectra

Ultraviolet properties of the compounds were published previously.[19]

(c) Nuclear magnetic resonance spectra

Nuclear magnetic resonance data, measured with a Varian HR-60 spectrophotometer at 60 Mc., for the bis(pentachlorophenyl) derivatives of the tri- and hexasilane, were consistent with the formulation $C_6Cl_5(SiMe_2)_nC_6Cl_5$. The spectrum of the trisilane showed two different methyl absorptions as singlets at 9.4 τ and 9.65 τ in the ratio of 2:1, the larger absorption being at the lower field. This splitting would be expected for a symmetrical, linear hexamethylated trisilane. The close proximity to the pentachlorophenyl groups of the methyl groups on the terminal silicon atoms would cause the greater chemical shift for the larger of the two absorptions, as observed. The spectrum of the hexasilane showed the anticipated three singlets of equal area, each resulting from the methyl groups on pairs of equivalent silicon atoms.

Attempted Reactions of the Pentachlorophenyl Compounds

(a) With magnesium

A reaction between pentachlorophenyltrimethylsilane and magnesium metal in tetrahydrofuran resulted in the formation of a Grignard reagent in high yield. Derivatization with chlorotrimethylsilane gave a brown gum which, when chromatographed on neutral alumina, yielded some white, low-melting crystals. These were not identified.

(b) On alumina

It has been found that basic alumina causes scission of the silicon-silicon bonds adjacent to a hydroxyl group in compounds such as 1,4-dihydroxyoctaphenyltetrasilane.[25] In an attempt to cause similar scission of bonds in the present pentachlorophenyl compounds, samples of 1,3-bis(pentachlorophenyl)hexamethyltrisilane in benzene as solvent were passed down alumina columns. Basic, acidic, and neutral alumina columns were tried, but in each case the unchanged polysilane was recovered quantitatively.

(c) Ultraviolet irradiation

As the pentachlorophenyl-substituted silanes have been shown to absorb ultraviolet irradiation to an appreciable extent[19] it was considered of interest to examine the effect of such irradiation on a solution of 1,2-bis(pentachlorophenyl)tetramethyldisilane. The irradiations were carried out in solutions of diethyl ether and isopropanol, the latter being an excellent radical trap. In neither case were any isolable products formed, and the starting material was recovered unchanged, essentially quantitatively.

B. EXPERIMENTAL

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. The glassware was dried in an oven at 130°C, assembled while hot, and purged with a stream of nitrogen. Tetrahydrofuran (THF) was dried over sodium wire. Chlorotrimethylsilane, dichlorodimethylsilane, and dichloromethylphenylsilane were obtained from the Dow Corning Corp. The α,ω-dichloropermethylated polysilanes,[26] the 1-H-3-chlorohexamethyltrisilane,[27] and 1,5-dichloro-[28] and α,ω-dibromoperphenylated polysilanes[30] were prepared according to previously described procedures. The acidic and neutral alumina were manufactured by Woelm, and purchased from Alupharm Chemicals, New Orleans, Louisiana: the basic alumina was obtained from Alcoa. Molecular weight determinations were made using a vapor pressure osmometer, Model 201A, manufactured by Mechrolab. Melting points and boiling points are uncorrected.

Pentachlorophenyltrimethylsilane

A solution of pentachlorophenylmagnesium chloride (0.1 mole) in THF was added dropwise over 60 min to chlorotrimethylsilane (10.9 g, 0.10 mole) in THF (50 ml). After the addition a Color Test I[17] was negative, and the dark brown mixture was stirred overnight at room temperature before hydrolysis with dilute hydrochloric acid. The organic material was extracted into diethyl ether, and the aqueous portion discarded. Removal of the ether gave the crude product, m.p. 100-108°C, (20.0 g). Recrystallization from petroleum ether (b.p. 60-70°C) gave 17.0 g (52%) of a white, crystalline solid, m.p. 116-117°C.

Anal. Calcd. for $C_9H_9Cl_5Si$: Si, 8.7%; mol. wt., 322.5. Found: Si, 9.3%; mol. wt., 322.

Bis(pentachlorophenyl)dimethylsilane

Using a procedure essentially the same as that described above, pentachlorophenylmagnesium chloride (0.10 mole) was caused to react with dichlorodimethylsilane (6.5 g, 0.05 mole). The crude product (22.0 g), m.p. 216-222°C, was recrystallized from petroleum ether (60-70°C) to give 18.0 g (65%) of pure product, m.p. 232-234°C.

Anal. Calcd. for $C_{14}H_6Cl_{10}Si$: Si, 5.0%; mol. wt., 556.8. Found: Si, 5.5%; mol. wt., 565.

Bis(pentachlorophenyl)methylphenylsilane

A reaction was carried out between the Grignard reagent (0.10 mole) and dichloromethylphenylsilane (9.6 g, 0.05 mole) in THF. After hydrolysis and extraction the crude product (17.5 g), m.p. 60-80°C, was obtained. Recrystallization from petroleum ether (60-70°C) gave 12.0 g (32%) of pure product, m.p. 164-165°C.

Anal. Calcd. for $C_{19}H_8Cl_{10}Si$: Si, 4.55%; mol. wt., 618.9. Found: Si, 4.4%; mol. wt., 608.

1,2-Bis(pentachlorophenyl)tetramethyldisilane

Following the usual procedure, pentachlorophenylmagnesium chloride (0.10 mole) and 1,2-dichlorotetramethyldisilane (9.4 g, 0.05 mole) reacted together to give 21.0 g of crude product, m.p. 218-222°C. Recrystallization from toluene gave 19.0 g (62%) of a white, crystalline product, m.p. 223-224°C.

Anal. Calcd. for $C_{16}H_{12}Cl_{10}Si_2$: Si, 9.15%; mol. wt., 615.0. Found: Si, 9.2%; mol. wt., 615.

1,3-Bis(pentachlorophenyl)hexamethyltrisilane

A reaction between the Grignard reagent (0.10 mole) and 1,3-dichlorohexamethyltrisilane (12.3 g, 0.05 mole) resulted in the formation of 18.0 g of crude product, m.p. 150-158°C. Recrystallization from petroleum ether (60-70°C) gave 14.7 g (47%) of pure product, m.p. 165-166°C.

Anal. Calcd. for $C_{18}H_{18}Cl_{10}Si_3$: Si, 12.5%; mol. wt., 673.3. Found: Si, 12.8%; mol. wt., 686.

1,4-Bis(pentachlorophenyl)octamethyltetrasilane

By the usual procedure a reaction was carried out between the Grignard reagent (0.05 mole) and 1,4-dichlorooctamethyltetrasilane (7.6 g, 0.025 mole). The crude product (9.0 g), m.p. 130-134°C, was recrystallized from petroleum ether (60-70°C) to give 5.9 g (32%) of the pure product, m.p. 143-145°C.

Anal. Calcd. for $C_{20}H_{24}Cl_{10}Si_4$: Si, 15.4%; mol. wt., 731.3. Found: Si, 15.4%; mol. wt., 738.

1,5-Bis(pentachlorophenyl)decamethylpentasilane

The reaction between pentachlorophenylmagnesium chloride (0.0083 mole) and 1,5-dichlorodecamethylpentasilane (1.50 g, 0.00415 mole) gave 1.30 g of crude product, m.p. 115-119°C. Recrystallization from petroleum ether (60-70°C) gave 1.0 g (31%) of pure product, m.p. 129-130°C.

Anal. Calcd. for $C_{22}H_{30}Cl_{10}Si_5$: Si, 17.8%; mol. wt., 789.4. Found: Si, 17.6%; mol. wt., 774.

1,6-Bis(pentachlorophenyl)dodecamethylhexasilane

A reaction was carried out in the usual manner between the Grignard reagent (0.062 mole) and 1,6-dichlorododecamethylhexasilane (13.0 g, 0.031 mole). The crude solid product (10.0 g), m.p. 138-142°C, which partially separated from the reaction mixture, was recrystallized from petroleum ether (60-70°C) to give 7.5 g (29%) of a white, crystalline product, m.p. 148-149°C.

Anal. Calcd. for $C_{24}H_{38}Cl_{10}Si_6$: Si, 19.9%; mol. wt., 847.6. Found: Si, 20.2%; mol. wt., 862.

Bis(pentafluorophenyl)dimethylsilane

Pentafluorophenyllithium (0.10 mole) was prepared in THF at *ca.* -65°C by an exchange reaction between *n*-butyllithium (supplied preformed in *n*-hexane by Foote Mineral Co., Exton, Pennsylvania) and bromopentafluorobenzene.[21] The solution, maintained at *ca.* -65°C, was divided into two equal portions. One half was added, from an addition funnel surrounded by Dry Ice, to dichlorodimethylsilane (3.23 g, 0.025 mole) over 45 min. Throughout the addition the temperature of the reaction mixture was kept at *ca.* -65°C. The mixture was then allowed to attain room temperature overnight, and hydrolyzed with dilute hydrochloric acid. Extraction with diethyl ether, followed by distillation, gave 6.8 g (70%) of a colorless liquid, b.p. 138-140°C/14 mm, shown by vapor phase chromatography to contain only one component.

Anal. Calcd. for $C_{14}H_6F_{10}Si$: Si, 7.15%; mol. wt., 392.3. Found: Si, 6.8%; mol. wt., 397.

1,3-Bis(pentafluorophenyl)hexamethyltrisilane

The second portion of pentafluorophenyllithium (0.05 mole) in THF, maintained at *ca.* -65°C, was added over 45 min to 1,3-dichlorohexamethyltrisilane (6.14 g, 0.025 mole). A similar reaction procedure was followed. Distillation gave 9.0 g (71%) of a colorless liquid, b.p. 116°C/0.07 mm, shown by vapor phase chromatography to be a single compound.

Anal. Calcd. for $C_{18}H_{18}F_{10}Si_3$: Si, 16.55%; mol. wt., 508.6. Found: Si, 16.4%; mol. wt., 500.

Attempted reactions of some α,ω-dihaloperphenylated polysilanes

(a) With pentachlorophenylmagnesium chloride

Coupling of the Grignard reagent in THF with 1,4-dichlorooctaphenyltetrasilane and 1,5-dichlorodecaphenylpentasilane was attempted by the usual procedure on a 0.05 mole scale. Even after the reaction mixtures had been refluxed for 24 hr, Color Test I[17] was positive in both cases, and hydrolyzed samples were shown by vapor phase chromatography to each contain pentachlorobenzene as the major component. In both cases the Color Test was negative after 2 days. Work-up by the usual method gave white solids which were identified as the α,ω-dihydroxy derivatives (mixed m.p.). Thus no reaction of the dichloro compounds would appear to have occurred until the final hydrolysis state.

(b) 1,4-Dichlorooctaphenyltetrasilane with pentachlorophenyllithium

The pentachlorophenyllithium was prepared in THF by an exchange reaction between *n*-butyllithium (0.05 mole) in *n*-hexane and hexachlorobenzene (14.24 g, 0.05 mole) following a procedure similar to that used for the preparation of pentafluorophenyllithium. To this lithium compound was added 1,4-dichlorooctaphenyltetrasilane (20.0 g, 0.025 mole). After 15 hr with the reaction mixture maintained at *ca.* -65°C, a Color Test I was still strongly positive, and pentachlorobenzene was the predominant product formed on hydrolysis of an aliquot (vapor phase chromatography). The temperature of the mixture was gradually raised, but the Color Test I persisted until the temperature had been at 0°C for 5 hr. A trace of pentachlorobenzene was still apparent. The residual pentachlorobenzene was still apparent. The residual solid (6.4 g) was filtered off and shown to be the unchanged dichloro compound (mixed m.p.). Following hydrolysis and extraction as usual, the diethyl ether was removed and petroleum ether (60-70°C) added. The solid thus formed (9.9 g), m.p. 170-188°C, was an unidentified mixture.

(c) Dibromo compounds with pentachlorophenyllithium

Reactions of 1,2-dibromotetraphenyldisilane and 1,4-dibromooctaphenyltetrasilane with pentachlorophenyllithium in THF were attempted following the usual general procedure. In both cases Color Test I was strongly positive after 20 hr with the reaction mixture at *ca.* -65°C, and pentachlorobenzene was predominant in hydrolyzed aliquots. Only after the reaction mixtures had been at 0°C for several hours did the Color Test give a negative result. No solid was apparent in either reaction mixture, and, following hydrolysis and extraction, no tractable products were isolated.

(d) 1,4-Dichlorooctaphenyltetrasilane with pentafluorophenyllithium

Pentafluorophenyllithium (0.05 mole), prepared in diethyl ether by the exchange reaction,[21] was added at *ca.* -65°C to 1,4-dichlorooctaphenyltetrasilane (20.0 g, 0.025 mole) over 60 min. The reaction mixture was maintained at *ca.* -65°C for 4 hr. After this time a Color Test I was still strongly positive, and the mixture was allowed to attain room temperature overnight. The Color Test was then negative. However, 19.5 g (98%) of the 1,4-dichlorooctaphenyltetrasilane was reclaimed (mixed m.p.), showing that reaction had taken place to a negligible extent.

Attempted reactions of 1-hydro-3-chlorohexamethyltrisilane

(a) With pentachlorophenylmagnesium chloride in THF

The Grignard reagent (0.10 mole) in THF was added over 2 hr to 1-hydro-3-chlorohexamethyltrisilane (21.09 g, 0.10 mole). A Color Test I was negative after a further hour, and the dark brown reaction mixture was hydrolyzed and extracted as usual. Removal of the solvent gave an intractable brown tar.

(b) With pentachlorophenylmagnesium chloride in diethyl ether

The Grignard reagent was prepared in diethyl ether using the modified entrainment method of Pearson *et al*,[24] and 0.01 mole of the solution added to 1-hydro-3-chlorohexamethyltrisilane (2.11 g, 0.01 mole) over 30 min. After 48 hr at room temperature, pentachlorobenzene was still the major component in a hydrolyzed aliquot of the reaction mixture (vapor phase chromatography). Only a trace of the pentachlorobenzene remained after the mixture had been refluxed for 36 hr. Following hydrolysis and extraction as usual, no tractable products were isolated.

(c) With pentachlorophenyllithium in THF

Pentachlorophenyllithium was prepared as usual in THF, and 0.01 mole of the solution added at *ca.* -65°C to 1-hydro-3-chlorohexamethyltrisilane (2.11 g, 0.01 mole) over 30 min. A Color Test I was negative after the addition. The reaction mixture was allowed to attain room temperature, and was then hydrolyzed and extracted. Removal of the solvent gave a yellow solid (0.7 g), m.p. 200-213°C. The infrared spectrum of this material showed broad bands characteristic of polymers, with no Si-H absorption. Attempts to recrystallize the solid were unsuccessful.

Attempts to prepare the di-Grignard reagent

(a) Using di-n-butyl ether as solvent

With di-n-butyl ether alone as solvent no reaction could be initiated between hexachlorobenzene and magnesium. When a little THF was added a reaction started, but no tetrachlorobenzene was apparent in a hydrolyzed aliquot of the reaction mixture (vapor phase chromatography). A second preparation of the Grignard reagent was carried out in THF alone as solvent. When the preparation was complete the THF was exchanged for di-n-butyl ether, and the resultant reaction mixture refluxed for 1 hr. Again no tetrachlorobenzene was apparent, and a Color Test I was negative. Hydrolysis and extraction of the mixture gave only a brown, unidentified tar.

(b) Using benzylmagnesium chloride

Benzylmagnesium chloride (0.085 mole) in THF was added dropwise to hexachlorobenzene (24.2 g, 0.043 mole) in an attempt to replace two chlorine atoms of the hexachlorobenzene with -MgCl. The reaction was exothermic, and the mixture turned dark blue; but a negligible amount of tetrachlorobenzene was apparent even after 24 hr.

Metalation of 1,2,4,5-tetrachlorobenzene

Preformed n-butyllithium (0.10 mole) in n-hexane was added over 40 min to 1,2,4,5-tetrachlorobenzene (5.9 g, 0.05 mole) in THF: the reaction mixture was maintained at -12±2°C. During the addition the color of the mixture turned from amber to dark brown, and 40 min after the addition a Color Test II[31] was negative, showing that all the n-butyllithium had reacted. Color Test I was still positive.

To this resultant solution was added chlorotrimethylsilane (10.9 g, 0.10 mole) in THF over 20 min, with the reaction mixture kept cool. After the addition a Color Test I was negative, and the mixture was maintained at ca. -12°C for 30 min before being allowed to attain room temperature. Hydrolysis and extraction as usual gave a dark red oil which solidified after standing under ethanol over the range 110-200°C, and could not be further purified or identified.

Reaction of magnesium with pentachlorophenyltrimethylsilane

Pentachlorophenyltrimethylsilane (6.44 g, 0.020 mole) was dissolved in THF, and part of the solution added to magnesium (0.5 g, 0.025 mole). A few drops of 1,2-dibromoethane rapidly initiated a reaction at room temperature, and the remainder of the silane was added over 30 min. The resultant dark brown solution was stirred overnight at room temperature. A positive Color Test I was then apparent, with a 74% yield of a Grignard reagent (acid/base titration). This reagent was decanted away from the residual magnesium, and added to chlorotrimethylsilane (1.52 g, 0.014 mole). After the addition a Color Test I was negative. The reaction mixture was stirred overnight before being hydrolyzed and extracted as usual. Removal of the solvent gave a brown gum containing a few crystals. The whole product was dissolved in petroleum ether (60-70°C) and chromatographed on neutral alumina which retained the brown material. A few white crystals, melting over the range 50-70°C, passed through the column; but these could not be further purified or identified.

Attempted cleavage of 1,3-bis(pentachlorophenyl)hexamethyltrisilane on alumina

A sample of 1,3-bis(pentachlorophenyl)hexamethyltrisilane (1.0 g) was dissolved in benzene, and passed down a small column packed with neutral alumina. Removal of the solvent from the fractions collected resulted in the total recovery of the starting material unchanged (mixed m.p.). The procedure was carried out using acidic and basic alumina; but in both cases the starting material was recovered quantitatively.

Ultraviolet irradiation of 1,2-bis(pentachlorophenyl)tetramethyldisilane

A slurry was made of 1,2-bis(pentachlorophenyl)tetramethyldisilane (2.0 g) in dry diethyl ether, and the mixture irradiated, in a quartz tube, by two low pressure mercury lamps at ca. 10 cm. from the quartz walls. Nitrogen was bubbled through the mixture. Irradiation was continued for 20 hr, and the ether then removed. The starting material was recovered quantitatively, unchanged (mixed m.p.).

A similar irradiation was carried out in isopropanol (dried and peroxides removed by distillation from calcium hydride: used immediately). The irradiation was continued for 4 days, but again no reaction occurred.

IV. POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS. THE PREPARATION OF SOME PENTAFLUOROPHENYL-SUBSTITUTED ORGANOSILICON COMPOUNDS

A. INTRODUCTION

Considerable interest has been shown recently in the preparation and properties of pentafluorophenyl derivatives of the elements.[32] However, relatively few derivatives of silicon have been reported. Tetrakis(pentafluorophenyl)-silane,[22,33] pentafluorophenyltrimethylsilane,[34,35] methyl-(pentafluorophenyl)diethoxysilane,[36] bis(pentafluorophenyl)-diethoxysilane,[36] pentafluorophenyldimethylsilane[36] and bis(pentafluorophenyl)methylsilane[36] were all prepared by the reaction of pentafluorophenylmetallic compounds with the corresponding chlorosilanes. In addition pentafluorophenyltrimethylsilane[37] was obtained from the reaction of bromopentafluorobenzene with bis(trimethylsilyl)mercury, and dichlorofluoropentafluorophenylsilane[35] and pentafluorophenyltrimethylsilane were obtained from the reactions of trichlorosilane and trimethylsilane with hexafluorobenzene under irradiation.

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

B. RESULTS AND DISCUSSION

Initial attempts were made to prepare pentafluorophenyltriphenylsilane, 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°C gave no detectable product 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°C as shown by v.p.c. However, on warming the reaction mixture to 20°C during three hours all the organometallic compound was consumed to give a mixture of products, from which was isolated compound I (12%), fluorotriphenylsilane (14%) and a large amount of material which did not melt below 450°C, although it softened at 350-400°C, 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 <u>et al</u>,[38] 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:

$$Ph_3SiCl + LiF \longrightarrow Ph_3SiF + LiCl$$

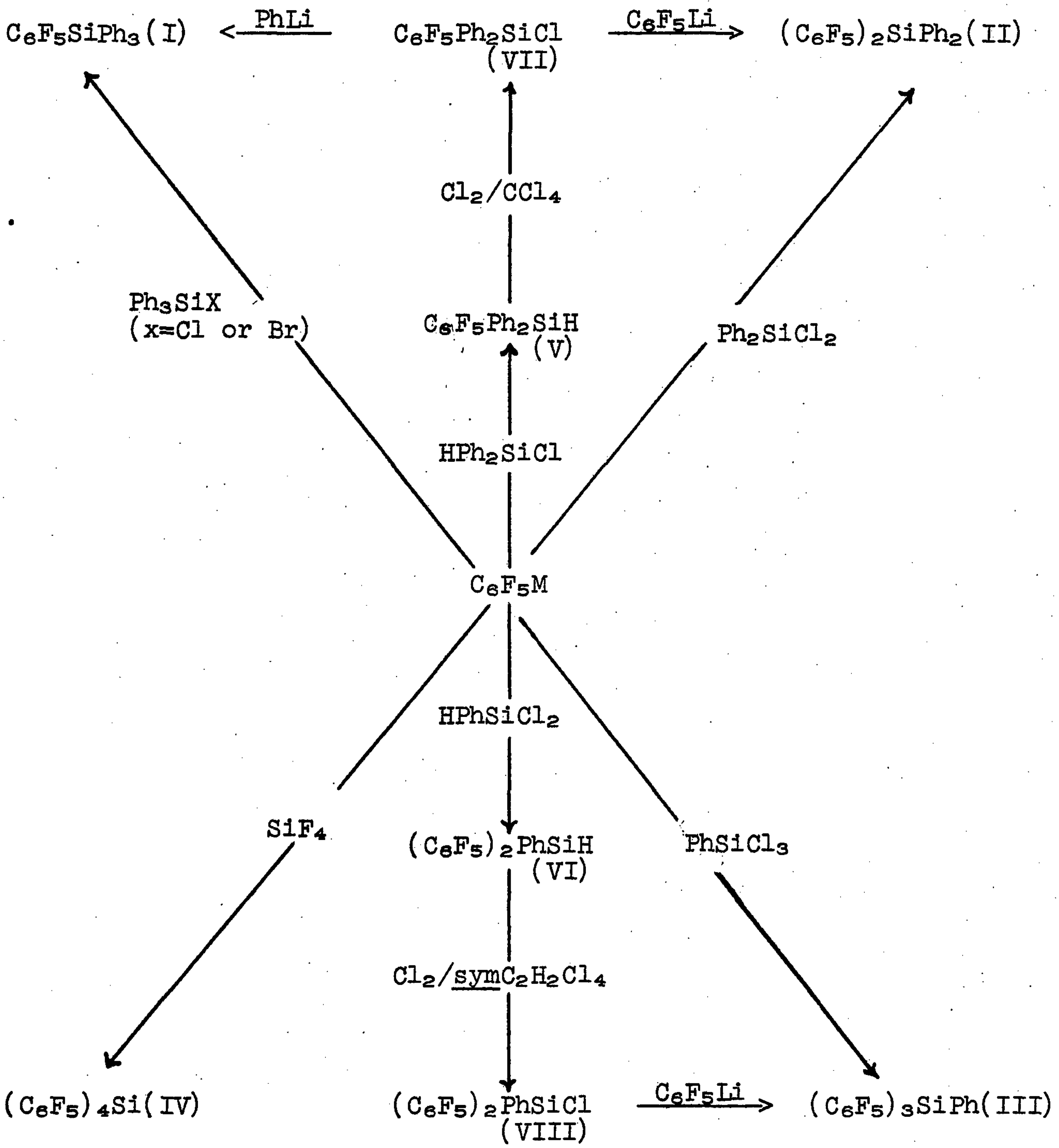
Similar yields of compound I (12.5%), fluorotriphenylsilane (14%) and "polymer" were obtained from the reaction of pentafluorophenylmagnesium bromide with chlorotriphenylsilane in THF. In this case the reaction only proceeded to an appreciable extent on heating the mixture to reflux for some hours.

The apparent reluctance of pentafluorophenylmetallic compounds to react with chlorotriphenylsilane is of interest for under similar conditions, pentachlorophenylmagnesium chloride[20] and pentachlorophenyllithium[39] react rapidly with chlorotriphenylsilane to give good yields of pentachlorophenyltriphenylsilane. This suggests that under the conditions used the pentafluorophenylmetallic compounds were less reactive than the corresponding pentachlorophenylmetallic compounds.

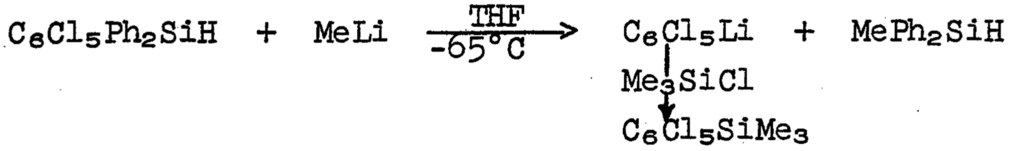
In an attempt to improve the yield of compound I the reaction of pentafluorophenyllithium in THF with bromotriphenylsilane was investigated. This reaction proceeded to completion at -65°C giving compound I in fair yield (48.4%) with the formation of much less fluorotriphenylsilane and polymer than was 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 (4 x moles) in THF at -65°C. 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 reported later.

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°C. However, the reactions were still slow and did not proceed to completion until warmed to room temperature.

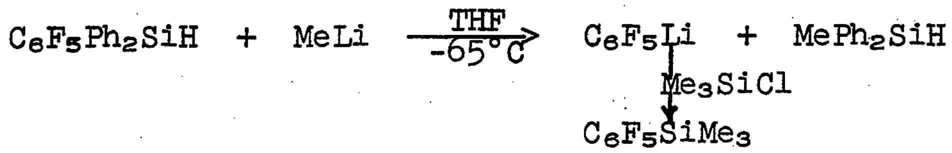

C₆F₅SiPh₃(I)
PhLi
C₆F₅Ph₂SiCl (VII)
C₆F₅Li
(C₆F₅)₂SiPh₂(II)
Cl₂/CCl₄
Ph₃SiX (x=Cl or Br)
C₆F₅Ph₂SiH (V)
Ph₂SiCl₂
HPh₂SiCl
C₆F₅M
HPhSiCl₂
SiF₄
(C₆F₅)₂PhSiH (VI)
PhSiCl₃
Cl₂/symC₂H₂Cl₄
(C₆F₅)₄Si(IV)
(C₆F₅)₂PhSiCl (VIII)
C₆F₅Li
(C₆F₅)₃SiPh(III)

It has been reported[41] that reaction of methyllithium with pentachlorophenyldiphenylsilane in THF at -65°C resulted in cleavage of the pentachlorophenyl group from silicon to give pentachlorophenyllithium and methyldiphenylsilane (37%). Chlorotrimethylsilane was used in this reaction to trap the pentachlorophenyllithium as pentachlorophenyltrimethylsilane in 29% yield:



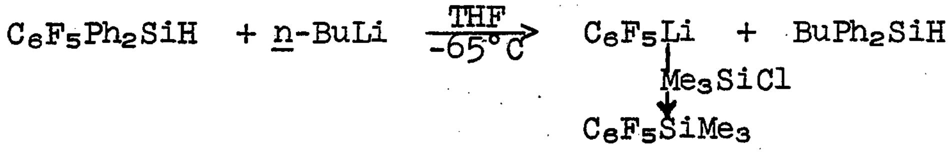
$$\begin{tikzcd} C_6Cl_5Ph_2SiH + MeLi \arrow[r, "THF", "-65^\circ C"'] & C_6Cl_5Li \arrow[d, "Me_3SiCl"] & + MePh_2SiH \\ & C_6Cl_5SiMe_3 & \end{tikzcd}$$

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 pentafluorophenyltrimethylsilane (44%) subsequent to derivatization with chlorotrimethylsilane, indicating that the pentafluorophenyl group had been cleaved from silicon as follows:



$$\begin{tikzcd} C_6F_5Ph_2SiH + MeLi \arrow[r, "THF", "-65^\circ C"'] & C_6F_5Li \arrow[d, "Me_3SiCl"] & + MePh_2SiH \\ & C_6F_5SiMe_3 & \end{tikzcd}$$

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



$$\begin{tikzcd} C_6F_5Ph_2SiH + \underline{n}\text{-}BuLi \arrow[r, "THF", "-65^\circ C"'] & C_6F_5Li \arrow[d, "Me_3SiCl"] & + BuPh_2SiH \\ & C_6F_5SiMe_3 & \end{tikzcd}$$

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 (2.65 τ), silicon-hydrogen (4.35 τ) and n-butyl (7.3, 8.5 and 9.05 τ), 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.

$$C_6F_5Ph_2SiH + \underline{n}\text{-}BuLi \longrightarrow \underline{n}\text{-}BuC_6F_4Ph_2SiH + LiF$$

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°C 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[33] to be characterized by the following absorptions: 1641 (m), 1516 (s), 1466 (s), 1379 (s), 1292 (s), 1140 (w), 1098 (s), 1023 (2), and 970 (s) cm^{-1}. The infrared spectra of all of the compounds prepared in this work were characterized 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.[42] 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 $C_6F_{5n}SiPh_{4-n}$, were recorded in cyclohexane. The absorptions are summarized in Table IV. 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[43] 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.

C. 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.[44] Silicon tetrafluoride was obtained from Matheson. Petroleum ether had a b.p. of 60-70°C. 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, v.p.c. analyses were carried out with an F and M Model 500 Gas Chromatograph using an 18 x 1/4" column packed with silicon gum rubber, SE 30, on Chromosorb W (1:20). All melting points are uncorrected.

Pentafluorophenylmetallic compounds

Pentafluorophenyllithium[21] 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[33] was prepared in THF by addition of bromopentafluorobenzene in THF to a slight excess of magnesium turnings.

The preparation of pentafluorophenyltriphenylsilane, I, by the reaction of pentafluorophenylmetallic 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°C. The mixture was stirred for 6 hr at -65°C when Color Test I[17] was still positive and v.p.c. showed the presence of much unreacted chlorotriphenylsilane. The mixture was allowed to warm to 20°C during 3 hr 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°C. 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°C/0.3 mm, m.p. 61-62°C (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 chromatographed over alumina. Elution with petroleum ether gave a white solid which was crystallized from pentane at -30°C to give compound I, m.p. 129-130°C (5.1 g, 12%). Found: C, 68.8; 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 hr stirring at room temperature no compound I could be detected by v.p.c., so the mixture was refluxed for 6 hr. 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°C. After 3 hr stirring at this temperature Color Test I was negative. Similar work-up 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 hr at -65°C when Color Test I was still slightly positive. The mixture was warmed to 20°C, concentrated, the residue extracted with petroleum ether and chromatographed over alumina. Elution with petroleum ether gave a white solid which was crystallized from pentane to give compound II, m.p. 151-152°C (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°C. After 5 hr stirring Color Test I was negative. The reaction mixture was warmed to 20°C. Compound III was isolated in a similar manner to compound II, as a white solid, m.p. 136-137°C (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

Silicaon 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°C (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°C. Color Test I was negative after 6 hr stirring at -65°C. 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°C/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, 51.71; 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°C. Color Test I was negative after 12 hr stirring at -65°C. Compound VI was isolated in a similar manner to compound V (0.1 g, 41.4%), b.p. 109-110°C/0.07 mm, n_D^{20} 1.5193. (Found: C, 49.6; H, 1.36; F, 42.8; mol. wt., 440. $C_{18}H_5F_{10}Si$ calcd.: C, 49.10; H, 1.36; F, 43.15%; mol. wt., 440.3).

Pentafluorophenyldiphenylchlorosilane, 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 hr no unreacted starting material could be detected by v.p.c. 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°C/0.6 mm, n_D^{20} 1.5591. (Found: C, 56.4; H, 2.8; F, 24.9; Cl, 9.4; mol. wt., 385. $C_{18}H_{10}F_5ClSi$ calcd.: C, 56.18; H, 2.60; F, 24.69; Cl, 9.22%; 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°C was added dropwise with stirring to diphenyldichlorosilane (12.5 g, 0.05 mole) in ether (50 ml) at -65°C. Color Test I was negative immediately after the addition when v.p.c. 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 recrystallized from pentane to give compound II, m.p. 149-151°C (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 hr no unreacted starting material could be detected by v.p.c. 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°C/0.05 mm, n_D^{20} 1.5270. (Found: C, 45.8; H, 0.98; Cl, 7.7; Si, 5.6; mol. wt., 475. $C_{18}H_5F_{10}ClSi$ 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°C and phenyllithium (0.078 mole) in ether (25 ml) was added. After stirring for 1 hr 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 recrystallized from pentane to give compound I, m.p. 129-130°C (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°C. Color Test I was negative after 3 hr. Identical work-up to that described above gave compound II, m.p. 149-151°C (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°C (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°C. The solution immediately turned purple and after 15 min v.p.c. 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 pentafluorophenyltrimethylsilane (2.1 g, 44%), b.p. 61-62°C/14 mm, n_D^{20} 1.4315 (Lit.[33] b.p. 60°C/14 mm, n_D^{20} 1.4331) and methyldiphenylsilane (2.4 g, 60.5%), b.p. 82-83°C/0.5 mm, n_D^{20} 1.5701 (Lit.[16] b.p. 79°C/0.1 mm, n_D^{20} 1.5694). The identity of these two compounds was confirmed by comparison of their infrared spectrum 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 pentafluorophenyltrimethylsilane (3.0 g, 41.7%), b.p. 63-64°C/15 mm, n_D^{20} 1.4317 and *n*-butyldiphenylsilane (4.1 g, 55.7%), b.p. 102-105°C/0.6 mm, n_D^{20} 1.5520 (Lit.[16] b.p. 110-112°C/1 mm, n_D^{20} 1.5541). In addition, 2.8 g of a liquid b.p. 147-150°C/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.

TABLE III

METHODS OF PREPARATION OF VARIOUS PENTAFLUOROPHENYL-SUBSTITUTED SILICON COMPOUNDS

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

TABLE IV

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

Compound n	Band Position max(mμ)	Molar Absorptivity
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 DK-2A spectrophotometer using cyclohexane as solvent.

[b] Shoulder.

V. THE REACTION OF TRIPHENYLSILYLMETALLIC COMPOUNDS WITH HEXAHALOBENZENES

A. DISCUSSION

As part of a general investigation into the preparation and comparison of properties of useful perhalophenyl-substituted organosilicon monomeric compounds, we wished to obtain pentafluorophenyltriphenylsilane, 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[45,46] or aryllithium[47] 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.

Triphenylsilyllithium (x moles) in THF was added to hexafluorobenzene (4 x moles) in THF at -65°C. A rapid reaction occurred but no compound I could be detected in the reaction mixture. The major products were hexaphenyldisilane, II (20.6%), and a solid m.p. 291-292°C, which appeared from elemental analysis, 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 isolated which did not melt below 430°C. The infrared spectra of this material indicated the presence of SiPh and C_6F_n moieties; it is possible that the material may be polymeric in nature.

The identity of compound III was confirmed by comparison with a sample prepared by the reaction of bromotriphenylsilane with 1,4-dilithiotetrafluorobenzene.[21]

Attempts to establish the origin of compound II have, so far, proved unsuccessful. Triphenylsilyllithium has frequently been shown to give high yields of this compound when treated with organic halides[2] and it has been established that the disilane arose via the following reaction sequence:

$$RX + Ph_3SiLi \longrightarrow RLi + Ph_3SiX$$

$$Ph_3SiLi + Ph_3SiX \longrightarrow Ph_6Si_2\ (II) + LiX$$

If a similar type of reaction occurred between triphenylsilyllithium and hexafluorobenzene, one of the products should be pentafluorophenyllithium:

$$C_6F_6 + Ph_3SiLi \longrightarrow Ph_3SiF + C_6F_5Li$$

$$Ph_3SiF + Ph_3SiLi \longrightarrow (Ph_3Si)_2(II) + LiF$$

However, all attempts to trap this intermediate have so far failed.

It has been shown[1] that reaction of triphenylsilylsodium with a variety of halogen compounds gave less of compound II than comparable reactions with triphenylsilyllithium. In the case of hexafluorobenzene this was not so, for reaction with triphenylsilylsodium under identical conditions to those used for triphenylsilyllithium gave compound II (33.4%) and compound III (19.8%).

Compound III was probably formed by a two stage reaction of triphenylsilyllithium with hexafluorobenzene:

$$C_6F_6 + Ph_3SiLi \longrightarrow Ph_3SiC_6F_5(I) + LiF$$

$$Ph_3SiC_6F_5(I) + Ph_3SiLi \longrightarrow Ph_3SiC_6F_4SiPh_3(III) + LiF$$

If this was so, it suggests that the presence of the triphenylsilyl-substituent in compound I activated the para-fluorine atom to nucleophilic attack, so that a further molecule of triphenylsilyllithium reacted at this position, rather than with the excess of hexafluorobenzene. This type of activation is becoming increasingly apparent as the number of examples of nucleophilic attack at hexafluoro- and substituted-pentafluorobenzenes, increase.[48]

The fact that the triphenylsilyl group does activate the para-fluorine atom of compound I to nucleophilic attack was demonstrated by treatment of compound I with triphenylsilyllithium at -65°C. An immediate reaction occurred to give compound III in 80.5% yield. No compound II was isolated from this reaction. Compound I, m.p. 129-130°C, was prepared by addition of bromotriphenylsilane to pentafluorophenyllithium in THF at -65°C.

In marked contrast to the above reactions, triphenylsilyllithium reacted with hexachlorobenzene in THF at -65°C predominately via an exchange reaction to give compound II (71.5%) and pentachlorophenyllithium. The presence of the latter compound was demonstrated by derivatization with chlorotrimethylsilane to give pentachlorophenyltrimethylsilane in 47% yield.

VI. THE REACTION OF n-BUTYLLITHIUM WITH PENTAFLUOROPHENYLTRIMETHYLSILANE

A. DISCUSSION

As part of a study on the general comparison of polyfluoro and polychloro compounds and on the preparation of tetrakis(trimethylsilyl)allene from polyfluorophenyl compounds,[49] it was necessary to prepare 1,4-bis(trimethylsilyl)tetrafluorobenzene, I. This compound was simply prepared in 81% yield by the Tamborski procedure from the reaction between 1,4-dilithiotetrafluorobenzene[21] and chlorotrimethylsilane. However, it had previously been shown in these laboratories[50] that 1,4-bis(trimethylsilyl)-tetrachlorobenzene could be prepared by the reaction of n-butyllithium (x moles) with pentachlorophenyltrimethylsilane (x moles) in THF at -65°C followed by treatment with chlorotrimethylsilane. It was of interest, therefore, to compare a similar series of reactions with pentafluorophenyltrimethylsilane as a possible route to compound I.

Addition of n-butyllithium in hexane to a solution of pentafluorophenyltrimethylsilane in THF at -65°C resulted in the consumption of all the organometallic species during 1 hour. Work-up gave a product, II, the n.m.r. spectrum of which contained an absorption at 9.6 τ characteristic of a trimethylsilyl group and absorptions at 7.3, 8.5 and 9.05 τ characteristic of an n-butyl group. The integrated area ratio of the trimethylsilyl to butyl protons was 1:1. This evidence, together with the molecular weight and elemental analysis, indicated that the compound contained a tetrafluorobenzene ring substituted by an n-butyl group and a trimethylsilyl group.

Treatment of II with 10% sodium hydroxide in THF at room temperature gave compound III, which appeared from its elemental analysis and molecular weight to be a butyl-substituted tetrafluorobenzene. The H^1 n.m.r. spectrum of compound III showed absorptions at 7.3, 8.5 and 9.05 τ characteristic of the n-butyl group and an absorption centered around 3.15 τ characteristic of an aromatic proton. The integrated area ratio of the aromatic to butyl protons was 1:9. The aromatic proton absorption at 3.15 τ was split into a symmetrical 9 line pattern of the type expected for an aromatic proton coupled with two ortho and two meta fluorine atoms. The observed coupling constants (J ortho F → H 10 c.p.s., J meta F → H 6 c.p.s.) were similar to those reported for this type of system.[51] This evidence suggested that compound III was n-butyl-2,3,5,6-tetrafluorobenzene and that compound II was therefore 1-trimethylsilyl-4-n-butyltetrafluorobenzene.

Experiments were then carried out to confirm rigorously the positions of the substituents. Treatment of 2,3,4,6-tetrafluorophenyllithium in ether or THF with an excess of n-butyl bromide gave no detectable quantity of compound III. However, this was not surprising as it has been reported[52] that treatment of 2,3,5,6-tetrafluorobromobenzene with n-butyllithium in ether gave 2,3,4,6-tetrafluorophenyllithium and, presumably, n-butyl bromide.

It has been shown that certain trialkyl phosphates frequently have advantages over the alkyl halides in the alkylation of organometallic compounds.[53] For this reason the reaction of 2,3,5,6-tetrafluorophenyllithium with tri-n-butyl phosphate at -65°C was investigated as a possible route to compound III. In ether, no alkylation appeared to occur as no compound III could be detected by v.p.c. even after the reaction mixture was allowed to warm to room temperature. However, when THF was used as solvent a 24% yield of compound III was obtained.

Compound III was converted to compound II in 70% yield by treatment with n-butyllithium in THF at -65°C followed by treatment with chlorotrimethylsilane.

The nucleophilic attack of an alkyllithium compound on a perfluorophenyl compound is not unusual. For instance, it has been shown that hexafluorobenzene reacts with methyllithium in THF[45] or ether[46] at low temperature to give 65-75% yields of pentafluorotoluene; a similar reaction[45] with n-butyllithium in THF gave 56% of n-butylpentafluorobenzene. It is therefore not surprising that compound II was obtained in 54% yield from the reaction of n-butyllithium with pentafluorophenyltrimethylsilane. However, the marked difference between pentafluorophenyltrimethylsilane and pentachlorophenyltrimethylsilane is of interest.

B. EXPERIMENTAL

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. Ethereal solvents were dried over sodium followed, in the case of THF, by distillation from sodium benzophenone ketyl. n-Butyllithium in hexane was obtained from Foote Mineral Corporation. Molecular weights were determined by mass spectrometry. N.m.r. spectra were recorded in CCl_4 with a Varian A60 spectrometer.

1,4-Bis(trimethylsilyl)tetrafluorobenzene

1,2,4,5-Tetrafluorobenzene (15 g, 0.1 mole) in THF (20 ml) was added to n-butyllithium (0.2 mole) in THF (270 ml) at -65°C. After 60 minutes Color Test II[31] was negative indicating that all the n-butyllithium had been consumed.

Chlorotrimethylsilane (21.7 g, 0.2 mole) in THF (50 ml) was added during 15 minutes, and Color Test I^{17} was negative immediately after the addition. The reaction mixture was allowed to warm to room temperature, concentrated, the residue extracted with petroleum ether (b.p. 60-80°), filtered and the residue concentrated leaving a white solid which on crystallization from methanol gave 1,4-bis(trimethylsilyl)tetrafluorobenzene, 24.8 g, 81.0%. Found: C, 49.3; h, 6.23; mol. wt., 294. $C_{12}F_4H_{18}Si_2$ calcd.: C, 49.0; H, 6.13%; mol. wt., 294.3.

Reaction of n-butyllithium with pentafluorophenyltrimethylsilane

n-Butyllithium (0.05 mole) in hexane was added to a solution of pentafluorophenyltrimethylsilane (12.0 g, 0.05 mole) in THF (75 ml) at -65°C. The solution turned slightly red and after 30 minutes Color Test I was negative. The reaction mixture was worked up as described above to give a liquid product which was distilled under reduced pressure to give 1-trimethylsilyl-4-butyl-tetrafluorobenzene, b.p. 77°C/0.6 mm, n_D^{20} 1.4595, 7.5 g, 54%. Found: C, 55.96; H, 6.74%; mol. wt. 278. $C_{13}F_4H_{18}Si_2$ calcd.: C, 56.1; H, 6.49%; mol. wt. 278.2.

Five g of the above material was dissolved in THF (25 ml) and 10% sodium hydroxide (5 ml) was added. The solution was stirred for 2 hours when v.p.c. showed that no starting material remained. The ethereal layer was separated, dried, concentrated and the residue distilled to give *n*-butyl-2,3,5,6-tetrafluorobenzene, b.p. 64°C/12 mm, n_D^{20} 1.4350, 2.9 g, 78.5%. Found: C, 58.6; H, 5.1%; mol. wt. 206. $C_{10}F_4H_{10}$ calcd.: C, 58.3; H, 4.9%; mol. wt. 206.1.

Reaction of 2,3,5,6-tetrafluorophenyllithium with tri-n-butyl phosphate

1,2,4,5-Tetrafluorobenzene (15 g, 0.1 mole) in THF (200 ml) was cooled to -65°C. *n*-Butyllithium (0.1 mole) in hexane was added dropwise with stirring during 1 hour. Color Test II was negative after the addition. A solution of tri-*n*-butyl phosphate (23.6 g, 0.1 mole) was added during 30 minutes. The reaction mixture was stirred 12 hours at -65°C when Color Test I was still positive. The reaction mixture was allowed to warm to room temperature during 5 hours, in which time it turned black, and Color Test I became negative. Following acid hydrolysis, the ethereal layer was dried, concentrated and the residue distilled to give 5.0 g, 24% of *n*-butyl-2,3,5,6-tetrafluorobenzene, b.p. 64-65°C/12 mm, n_D^{20} 1.4349.

Preparation of 1-trimethylsilyl-4-n-butyltetrafluorobenzene from n-butyl-2,3,5,6-tetrafluorobenzene

n-Butyl-2,3,5,6-tetrafluorobenzene (4 g, 0.02 mole) was dissolved in THF (50 ml) at -65°C and n-butyllithium (0.02 mole) was added during 5 minutes. Color Test II was negative immediately after the addition. Chlorotrimethylsilane (6 g, excess) was added and the mixture was allowed to warm to room temperature, before being concentrated and the residue treated with pentane and filtered. Concentration of the pentane solution and distillation of the residue under reduced pressure gave 3.9 g, 70% of 1-trimethylsilyl-4-n-butyltetrafluorobenzene, b.p. 70-71°C/0.2 mm, n_D^{20} 1.4593.

VII. TETRAKIS(TRIMETHYLSILYL)ALLENE FROM SOME PENTAFLUOROBENZENE AND TETRAFLUOROBENZENE DERIVATIVES

A. DISCUSSION

Work in these laboratories has shown[54] that reaction of hexachlorobenzene, trimethylsilylpentachlorobenzene, or 1,4-di(trimethylsilyl)tetrachlorobenzene, with a liberal excess of chlorotrimethylsilane and lithium in THF gives the unexpected tetrakis(trimethylsilyl)allene,[54,55] I, in 30-52% yields.

$$(Me_3Si)_2C{=}C{=}C(SiMe_3)_2 \qquad (I)$$

However under similar conditions hexafluorobenzene, in marked contrast, did not react.

In an extension of the above work we have found that bromopentafluorobenzene, chloropentafluorobenzene, trimethylsilylpentafluorobenzene and 1,4-di(trimethylsilyl)-tetrafluorobenzene all give I in 6-10% yields when treated under the above conditions. In addition, hexamethyldisilane and fluorotrimethylsilane have been identified as products of these reactions, all compounds being identified by spectroscopic comparison with authentic materials.

Work is currently in progress to establish the mode of formation of compound I from the perchloro and perfluoro compounds. Possible reactive intermediates being considered include perhalo-substituted benzynes and anion-radicals.[56] In preliminary attempts to demonstrate the presence of highly reactive[57] benzyne intermediates the reactions of hexachlorobenzene and chloropentafluorobenzene were carried out in 50% THF/furan. The reactions proceeded extremely slowly compared with reactions in the absence of furan, and no compound I could be detected. The only products so far identified were small amounts of the respective trimethylsilylpentahalobenzenes, $Me_3SiC_6X_5$.

At the present time it would appear that the fluorotrimethylsilane isolated from the perfluorobenzene reactions may have been largely formed by reaction of chlorotrimethylsilane with lithium fluoride liberated during the course of the reaction. However, as it has been shown that a trimethylsilyl radical can abstract halogen atoms from a halobenzene,[58] the possibility that a trimethylsilyl radical abstracted fluroine from the perfluorinated compound cannot be excluded at this stage.

VIII. THE PREPARATION OF SOME ORGANOSILICON-SUBSTITUTED POLYHALODIPHENYLALKANES

A. INTRODUCTION

The primary objective of the work described in this report is the preparation of novel and useful monomers containing polyfluoro or polychloro groups which can be used to prepare polymers having useful properties such as high thermal stability. A series of stepwise reactions was examined to find the preferred synthesis, scope and limitations for the preparation of monomers of the type

$$H(CH_3)_2SiC_6X_4(CY_2)_nC_6X_4Si(CH_3)_2H$$

where X = F, Cl; Y = H, F, Cl; and n = 4, 5, 6.

The obvious route to the above compounds seemed to be via the preparation of compounds of the type

$$C_6X_5(CY_2)_nC_6X_5$$

B. DISCUSSION

α,ω-Bis(pentachlorophenyl)alkanes

The only route to compounds of this type seemed to be via reaction of pentachlorophenyllithium[59] or pentachlorophenylmagnesium chloride[60] with various α,ω-dibromoalkanes. Only one other reaction of this type has previously been reported:[61] the reaction of two 2-lithio-1,3-dithianes with 1,3-dibromopropane (66% yield) and 1,4-dibromobutane (84% and 89% yields).

It was found that phenyllithium reacted with a variety of bromo- and iodoalkanes, including 1,2-dibromoethane, by Li/Halogen exchange. The coupling product was not obtained.[62]

$$C_6H_5Li + BrCH_2CH_2Br \longrightarrow C_6H_5Br + LiCH_2CH_2Br$$

This metathesis was not observed in the reactions of pentachlorophenyllithium and, later, of pentafluorophenyllithium, with α,ω-dihaloalkanes and iodoalkanes. As mentioned later, diiodomethane seems to be an exception to this rule.

A small scale reaction of pentafluorophenyllithium (5 x moles) with diiodomethane (2 x moles) did not yield any bis(pentafluorophenyl)methane.[85] Distillation of the product afforded a small quantity of a liquid which obviously contained an iodo-compound, insufficient to characterize but possibly pentafluoroiodobenzene. Analysis by VPC indicated that no diiodomethane remained and possibly, that pentafluorobenzene was present in the solvent fraction. This result indicates that the major reaction is H/Li exchange with the formation of transient diiodomethyllithium or dilithiodiiodomethane, and accompanied by some I/Li exchange. Many reactions of this type have been reported for bromo- and chloro-compounds.[77]

Compounds of the type p-$(CH_3)_3SiC_6F_4(CH_2)_nC_6F_4Si(CH_3)_3$-p

These compounds were required as models in later reactions of compounds of the type p-$HC_6F_4(CH_2)_nC_6F_4H$-p to obtain reactive monomers of the type p-$H(CH_3)_2SiC_6F_4(CH_2)_nC_6F_4Si(CH_3)_2H$-p.

Previous workers found that n-butyllithium reacted with trimethylpentafluorophenylsilane to give 1-butyl-4-trimethylsilyltetrafluorobenzene in good yield without cleavage of the silicon-C_6F_5 bond[86] as observed with some other pentafluorophenyl-silicon compounds.[87] Reaction of 1,4-dilithiobutane, 1,5-dilithiopentane, and 1,6-dilithiohexane in ether with trimethylpentafluorophenylsilane gave good yields of the respective α,ω-bis(4′-trimethylsilyltetrafluorophenyl)-alkanes.

Cleavage of the silicon-pentafluorophenyl bond by sodium hydroxide in THF should yield the respective α,ω-bis(2,3,5,6-tetrafluorophenyl)alkane, which could also be prepared by reaction of α,ω-bis(pentafluorophenyl)alkanes with hydrazine in dioxan, followed by dehydrazination of the product with hot aqueous copper sulphate.[88] Work is in progress along this line. The reaction between 2,3,5,6-tetrafluorophenyllithium and 1,5-diiodopentane to obtain 1,5-bis(2′,3′,5′,6′-tetrafluorophenyl)pentane is at present under investigation.

Reaction of organolithium compounds with 1,6-dibromododecafluorohexane

Although there are many reports of exchange reactions occurring between organometallic reagents and perfluoroalkyl iodides[88] few have been reported with the bromides.

$$\underline{n}\text{-}C_3F_7I + C_6H_5MgBr \xrightarrow[-40^\circ]{Et_2O} \underline{n}\text{-}C_3F_7MgBr + C_6H_5I$$

$$\underline{n}\text{-}C_3F_7I + RLi \xrightarrow{Et_2O} \underline{n}\text{-}C_3F_7Li + RI$$

The perfluoroalkylorganometallic compounds are not stable and decompose via α-elimination of metal fluoride, hydrogen abstraction from solvent, or polymerisation or a combination of all three.

An exchange reaction occurred on addition of 1,6-dibromododecafluorohexane (x moles) to pentachlorophenyllithium (2 x moles) in THF at -70°C and bromopentachlorobenzene was isolated in 50% yield, identical to a sample kindly supplied by Dr. C. Tamborski. Analysis by VPC indicated that none of the dibromohexane remained, and no 1,6-bis(pentachlorophenyl)dodecafluorohexane could be isolated from the residues. Pentafluorophenyllithium did not appear to react with the above 1,6-dibromododecafluorohexane. In a small scale experiment no bromopentafluorobenzene could be detected by VPC, and a 44% recovery of 1,6-dibromododecafluorohexane was made, together with some insoluble, high melting point solid presumably from the decomposition of pentafluorophenyllithium.

Attempted preparation of 1,6-dilithiododecafluorohexane and reaction with hexafluorobenzene

Despite the fact that perfluoroalkyllithium compounds are very unstable, they have been reacted with many carbonyl compounds and chlorosilanes[89] to yield the expected products. Only one α,ω-dilithioperfluoroalkane has been reported:[90] 1,4-dilithiooctafluorobutane. The latter was prepared and derivatised in 18% yield by alternate addition of n-butyllithium and acetaldehyde to 1,4-diiodooctafluorobutane in ether at -80 to -85°C. By a similar method n-butyllithium (2 x moles) in hexane and hexafluorobenzene (2 x moles) in THF were added alternately to 1,6-dibromododecafluorohexane (x moles) in THF at -78°C. THF was employed as solvent in the hope that the organolithium compound would be more reactive towards hexafluorobenzene in this solvent rather than ether. However, the only product was a low weight recovery of a liquid of low boiling point which contained two components by VPC, one apparently being 1,6-dibromododecafluorohexane. No butylpentafluorobenzene was formed. Evidently the n-butyllithium had reacted with most of the 1,6-dibromohexane but the organolithium compound formed had decomposed.

Attempted preparation of 1,2-dilithiotetrachloroethane and reaction with hexafluorobenzene

Addition of n-butyllithium (2 x moles) in hexane to 1,1,2,2-tetrachloroethane (x moles) in mixed solvents[77] at -105°C followed by addition of excess hexafluorobenzene did not yield any 1,2-bis(pentafluorophenyl)tetrachloroethane, nor was any 1,1,2,2-tetrachloroethane recovered. This indicates that an organolithium compound was formed but decomposed.

Work is in progress on a similar reaction with 1,6-dibromododecafluorohexane in the hope that 1,6-dilithiododecafluorohexane will be stable at this temperature, and will react with hexafluorobenzene.

C. EXPERIMENTAL

1,4-Bis(pentachlorophenyl)butane

(a) From pentachlorophenylmagnesium chloride

To pentachlorophenylmagnesium chloride,[60] prepared from hexachlorobenzene (28.5 g, 0.1 mole) and excess magnesium (9.7 g), in THF (150 ml) was added 1,4-dibromobutane (10.0 g, 0.046 mole) and the solution stirred for 3 days at room temperature, when no pentachlorobenzene or 1,4-dibromobutane could be detected in a hydrolysed portion of the reaction mixture by GLC. After addition of dilute hydrochloric acid, a brown solid was filtered off, and the THF layer was separated and dried ($MgSO_4$). The residue left by evaporation of the solvent and the dried solid were chromatographed on silica gel in CCl_4. Concentration and crystallisation of the eluant afforded crude 1,4-bis(pentachlorophenyl)butane as a pale yellow solid (10.46 g, m.p. 210.5-213.5°C and 3.16 g, m.p. 201-206°C, crude yield 48.7%). Recrystallisation afforded a pale yellow solid (10.9 g, 39%) m.p. 220-221°C. (Found: C, 34.76; H, 1.60; C, 34.95; H, 1.79%; mol. wt. 554. $C_{16}H_8Cl_{10}$ calcd.: C, 34.64; H, 1.45%; mol. wt. 554.8.) Another fraction was obtained by chromatography, which on evaporation afforded a red oil (8.7 g) which could not be crystallised, or identified.

(b) From pentachlorophenyllithium

Pentachlorophenyllithium[59] was prepared by addition of n-butyllithium (0.1 mole) in hexane (62.5 ml) dropwise over 18 minutes to hexachlorobenzene in THF (100 ml) at -70°C. After stirring for a further 1.5 hr at -70°C, when Color Test I[17] was positive and Color Test II[31] negative, 1,4-dibromobutane (10.3 g, 0.047 mole) was added and the mixture continually stirred at -70°C. Color Test I was negative after 5 hr. After addition of dilute hydrochloric acid a buff solid (20 g) was filtered off. The solvent layer was separated, dried ($MgSO_4$), and evaporated to dryness. Crystallisation of the dried solid and residue from CCl_4 afforded pale yellow 1,4-bis(pentachlorophenyl)butane (9.04 g, m.p. 213-214°C, and 6.93 g, m.p. 190-193°C; crude yield 57%). Recrystallisation gave 12.5 g (44%), m.p. 220-221°C, identical to that obtained from pentachlorophenylmagnesium chloride and 1,4-dibromobutane.

IR spectrum (CCl_4): 2940 (w), 1465 (w), 1373 (s), 1360 (s), 1316 (w), 1293 (w), 1230 (w), 1115 (m), and 667 (m) cm^{-1}.

1,5-Bis(pentachlorophenyl)pentane

(a) From pentachlorophenylmagnesium chloride

To pentachlorophenylmagnesium chloride,[60] prepared from hexachlorobenzene (28.5 g, 0.1 mole) and excess magnesium in THF (150 ml), was added 1,5-dibromopentane (9.2 g, 0.04 mole) and the mixture stirred at room temperature for 28 hr when GLC indicated that the reaction was complete. The mixture was worked up as before, affording 1,5-bis(pentachlorophenyl)-pentane as a white solid (6.1 g, m.p. 202-204°C, and 4.77 g, m.p. 198-199°C, crude yield 38%). Recrystallisation from the same solvent gave a white solid (10.0 g), m.p. 204.5-205°C. (Found: C, 35.77; H, 1.67; C, 35.82; H, 1.84%; mol. wt. 567. $C_{17}H_{10}Cl_{10}$ calcd.: C, 35.89; H, 1.77%; mol. wt. 568.8).

(b) From pentachlorophenyllithium

To pentachlorophenyllithium,[59] prepared as before in THF from hexachlorobenzene (28.5 g, 0.1 mole), at -70°C was added 1,5-dibromopentane (11.5 g, 0.05 mole). Color Test I was negative within 5 hr. Work-up as before afforded 1,5-bis(pentachlorophenyl)pentane as a white solid (12.95 g, yield 45.5%), m.p. 203-205°C. Recrystallisation from the same solvent gave 11.52 g, m.p. 204.5-205°C, identical to a sample prepared *via* the Grignard reagent.

IR spectrum (CCl_4): 2940 (w), 1462 (w), 1373 (s), 1360 (s), 1316 (w), 1116 (m), and 667 (s) cm^{-1}.

1,6-Bis(pentachlorophenyl)hexane

(a) From pentachlorophenylmagnesium chloride

To pentachlorophenylmagnesium chloride,[60] prepared from hexachlorobenzene (28.5 g, 0.1 mole) in THF (130 ml), was added 1,6-dibromohexane (9.76 g, 0.04 mole) and the solution stirred at ambient temperatures for 3.5 days. Work-up as before gave a buff solid (12.3 g), m.p. 210-212°C. Crystallisation from CCl_4 afforded a pale yellow solid (10.38 g, 35% crude) m.p. 214-216°C. The pure material has m.p. 219-

219.5°C, and was identified as 1,6-bis(pentachlorophenyl)-hexane by molecular weight determination and infrared spectroscopy.

IR spectra (CCl_4): 2925 (m), 1360 (w), 1370 (s), 1356 (s), 1315 (w), 1230 (w), 1115 (m), and 667 (s) cm^{-1}. ($C_{18}H_{12}Cl_{10}$: mol. wt. 582.8. Found: 583).

(b) From pentachlorophenyllithium

To pentachlorophenyllithium,[59] prepared by addition of n-butyllithium (0.1 mole) to hexachlorobenzene (28.5 g, 0.1 mole) in THF (140 ml) at -70°C, was added 1,6-dibromohexane (10.98 g, 0.045 mole). Color Test I was negative after 5 hrs. Work-up as before gave a buff solid (24.9 g), m.p. 210-212°C. Crystallisation of this solid from CCl_4 gave a pale yellow solid (17.50 g, crude yield 60%), m.p. 214-216.5°C. A pure sample was obtained by further crystallisation identical to that previously obtained via the Grignard reagent and identified as 1,6-bis(pentachlorophenyl)hexane.

1,3-Bis(pentachlorophenyl)propane

To pentachlorophenylmagnesium chloride, prepared from hexachlorobenzene (28.5 g, 0.1 mole) in THF (150 ml) by a published procedure,[61] was added 1,3-dibromopropane (8.08 g, 0.04 mole) and the solution stirred at ambient temperatures for 3.5 days. After hydrolysis with dilute hydrochloric acid a brown solid (6.02 g), m.p. 249-254°C, was filtered from the THF layer, which was then dried ($MgSO_4$). The solid was dried in vacuo over phosphoric oxide and crystallised twice from xylene, and then benzene to give yellow crystals (3.37 g), m.p. 257-257.5°C.

The IR spectrum (CCl_4 soln.) indicated that this material was 1,3-bis(pentachlorophenyl)propane as peaks were observed at 2930 cm^{-1} (alkyl C-H), 1358, 1210 and 677 cm^{-1}, and the spectrum was very similar to those of other α,ω-bis(pentachlorophenyl)alkanes.

The THF was distilled off and the oily residue chromatographed on a column of silica gel in CCl_4. A yellow, unidentified, viscous oil (12.55 g) was obtained, but no crystalline solid as above.

Attempted reaction of pentachlorophenyllithium with 1,4-dichlorobutane

Pentachlorophenyllithium was prepared by addition of n-butyllithium (0.1 mole) in hexane (62.5 ml) to hexachlorobenzene (28.5 g, 0.1 mole) in THF (100 ml) at -70°C over 30 minutes and stirring at this temperature for a further 2.5 hr. 1,4-Dichlorobutane (5.72 g, 0.045 mole) was added and the mixture stirred at -70°C for 17 hrs. Color Test I was still positive after this time. The temperature was allowed to rise to -50°C over a further 9.5 hr, and -20°C over a further 14.5 hr, by which time Color Test I was negative. After addition of dilute hydrochloric acid, the red THF layer was separated, dried ($MgSO_4$), and the solvent evaporated. The residual oil was distilled under reduced pressure to yield 1,4-dichlorobutane (1.16 g, 20%), identified by infrared spectroscopy, and a white solid (3.8 g), m.p. 211-216°C. Crystallisation of this solid from light petroleum (b.p. 60-70°C) gave slightly impure hexachlorobenzene (2.9 g), m.p. 216-218°C as identified by infrared spectroscopy. The residues from the distillation were chromatographed on a silica gel column in CCl_4 to give an unidentified red oil (13.17 g). No 1,4-bis(pentachlorophenyl)butane was isolated.

1,4-Bis(4-trimethylsilyltetrachlorophenyl)butane

(a) From 1,4-bis(pentachlorophenyl)butane

To 1,4-bis(pentachlorophenyl)butane (12.0 g, 0.021(5) mole) in THF (150 ml) at -70°C was added *n*-butyllithium (0.048 mole) in hexane (30 ml) dropwise over 15 minutes and the mixture stirred at -70°C for a further 1.5 hr, by which time Color Test II was negative and Test I positive. Chlorotrimethylsilane (5.85 g, 0.054 mole) was added, and Color Test I was negative within three hrs. After evaporation to dryness, the residual gum was extracted with CCl_4 and the extract evaporated. Crystallisation of the residual oil from petroleum ether (b.p. 60-70°C) gave a white solid (2.83 g), m.p. 136-139°C. Recrystallisation twice from the same solvent afforded 1,4-bis(pentachlorophenyl)butane (0.4 g), m.p. 218-220°C, and 1,4-bis(4-trimethylsilyltetrachlorophenyl)butane (A) (2.0 g), m.p. 151.5-152°C. The residue was dissolved in hot absolute ethanol and decanted from an oil (1.92 g) which solidified on cooling to a hard, toffee-like mass. Evaporation of the solvent followed by chromatography in light petroleum (b.p. 60-70°C) on silica gel afforded compound A (6.49 g), m.p. 140-142°C (total crude yield 66%). ($C_{22}H_{26}Cl_8Si_2$: mol. wt. 630.2. Found: 630.)

(b) From pentachlorophenyltrimethylsilane

To pentachlorophenyltrimethylsilane (11.5 g, 0.036 mole) in THF (80 ml) at -70°C was added *n*-butyllithium (0.04 mole) in hexane (25 ml), dropwise over 10 minutes, and the mixture stirred for a further 45 minutes at -70°C, by which time Color Test II was negative and Color Test I positive. 1,4-Dibromobutane (3.8 g, 0.018 mole) in pentane (20 ml) was added slowly and the mixture kept at -70°C for 26 hours, by which time Color Test I seemed to be negative, and then allowed to warm up slowly to room temperature over 14 hrs. The solvents were evaporated and the residual gum extracted with hot petroleum ether (b.p. 60-70°C). Concentration of the extract afforded a white solid (2.5 g), m.p. 132-138°C, which on recrystallisation five times from the same solvent gave a white solid, m.p. 151-151.5°C, identical to compound A (mixed m.p. 151.5-152°C). The residues were dissolved in hot absolute ethanol and decanted from a gum (0.9 g) which solidified on cooling to a hard, toffee-like mass. The ethanolic solution on cooling deposited a further quantity of a sparingly soluble gum (1.67 g). Evaporation of the solvent followed by chromatography on a column of silica gel in petroleum ether (b.p. 60-70°C) afforded a white solid (2.6 g), m.p. 139-141°C, shown by infrared spectroscopy to be slightly impure compound A.

α,ω-Dilithioalkanes

1,4-Dilithiobutane, 1,5-dilithiopentane, and 1,6-dilithiohexane were prepared in ether by a published procedure,[69] except that lithium wire (100 cm weighing 4.3 g) cut into pieces 1/8" long was used instead of fine lithium shot. 1,4-Dibromobutane (64.79 g, 0.30 mole) gave a 0.37 M solution of 1,4-dilithiobutane corresponding to 46% conversion. Allyl bromide was employed in standardisation of these solutions by the method of Gilman and Cartledge.[9]

1,5-Dibromopentane (34.5 g, 0.15 mole) afforded a 0.58 M solution of 1,5-dilithiopentane, corresponding to 85% conversion.

1,6-Dibromohexane (61.0 g, 0.25 mole) afforded a 0.27 M solution of 1,6-dilithiohexane, corresponding to 48% conversion. Titration indicated that this preparation had a high base content, and, unlike the two previous preparations, which gave clear solutions, a large quantity of a pink solid which would not settle.

1,4-Bis(pentafluorophenyl)butane

1,4-Dilithiobutane (0.10 mole) in ether (280 ml) was added to hexafluorobenzene (55.8 g, 0.3 mole) in ether (130 ml) over 45 minutes at 15-20°C. Color Test I was negative after stirring for a further two hours. The reaction mixture was worked up as before. Distillation afforded two colorless liquids, b.p. 75-100°C/16 mm and b.p. 100-160°C/16 mm, and a colorless liquid (23.98 g) b.p. 160-195°C/16 mm, which solidified, m.p. 65.5-68°C. Crystallisation from pentane afforded white crystals, m.p. 72.5-73.5°C, which were identified as 1,4-bis(pentafluorophenyl)butane. The crude yield was 61% based on 1,4-dilithiobutane.

IR spectrum (CCl_4): 2950 (s), 2850 (m), 1730 (w), 1657 (s), 1492 (s), 1465 (s), 1427 (s), 1342 (s), 1300 (s), 1167 (m), 1126 (s), 1092 (w), 1064 (w), 990 (s), 950 (m), 915 (m), 892 (m), and 870 (w) cm^{-1}. ($C_{16}H_8F_{10}$: Mol. wt. 390.2. Found: 390.)

1,5-Bis(pentafluorophenyl)pentane

Small aliquots of a solution of 1,5-dilithiopentane (0.05 mole) in ether (87 ml) were added to a stirred solution of hexafluorobenzene (22.33 g, 0.12 mole) in ether (100 ml) at -15°C. As no precipitation of lithium fluoride was observed the temperature was raised to +15°C during the remainder of the addition. Within four hours Color Test I was negative. The mixture was worked up in the usual manner. After distilling off the solvents the residual liquid was distilled under reduced pressure to give three fractions: (i) a colorless liquid (0.7 g); (ii) a colorless liquid (12.15 g), b.p. 188-189°C/22 mm Hg, which solidified to give a white solid, m.p. 52-53°C; (iii) a colorless liquid (1.08 g), distilling at 0.1-0.2 mm Hg. A residual liquid (3.1 g) solidified on cooling.

Distillation of the solvents afforded a fraction containing hexafluorobenzene (3.5 g) by GLC.

Fraction (ii) was crystallized from pentane, affording 1,5-bis(pentafluorophenyl)pentane, m.p. 56-56.5°C.

IR spectrum (CCl_4): 2925 (m), 2850 (w), 1650 (m), 1498 (s), 1458 (w), 1420 (w), 1296 (w), 1152 (m), 1120 (s), 1102 (m), 964 (s), 956 (m), and 885 (w) cm^{-1}. ($C_{17}H_{10}F_{10}$: mol. wt. 404.2. Found: 404.)

1,6-Bis(pentafluorophenyl)hexane

1,6-Dilithiohexane (0.11 mole) in ether was added to hexafluorobenzene (40.9 g, 0.22 mole) in ether (50 ml) at 25°C over 45 minutes while stirring. Color Test I was negative within 10 minutes of completion of addition of 1,6-dilithiohexane. Work-up in the usual manner, followed by distillation under reduced pressure, afforded: (i) a colorless liquid (1.08 g) containing two components by VPC; (ii) a colorless liquid (16.5 g), b.p. 136-140°C/0.05 mm, which solidified m.p. 51.5-52.5°C; and (iii) a pale yellow liquid (2.5 g), b.p. 200-220°C/0.05 mm. Involatile residues (16.65 g) solidified on cooling. Fraction (ii), on crystallisation from pentane gave white crystals, m.p. 56-56.5°C, identified as 1,6-bis(pentafluorophenyl)hexane by infrared spectroscopy.

IR spectrum (CCl_4): 2930 (m), 2850 (w), 1651 (m), 1494 (s), 1464 (w), 1424 (w), 1304 (w), 1148 (m), 1118 (s), 962 (s), and 943 (s) cm^{-1}.

1,4-Bis(4′-trimethylsilyltetrafluorophenyl)butane

1,4-Dilithiobutane (0.026 mole) in ether (70 ml) was added to trimethylpentafluorophenylsilane (12.5 g, 0.052 mole) in ether (25 ml) over 25 minutes at 15-20°C. Within three hours Color Test I was negative. Work-up in the usual manner, followed by distillation under reduced pressure gave: (i) a colorless liquid (2.58 g), b.p. 70-72°C/0.1 mm, containing two components, one with an identical VPC retention time to 1-butyl-4-trimethylsilyltetrafluorobenzene; (ii) a liquid (0.81 g) containing fractions (i) and (iii); (iii) a colorless liquid (6.55 g, crude yield 52.5%), b.p. 170-175°C/0.1 mm which solidified on cooling, m.p. 75.5-76.5°C and identified by infrared spectroscopy as 1,4-bis(4′-trimethylsilyltetrafluorophenyl)butane. Crystallisation from hexane afforded white crystals, m.p. 80.5-81.5°C.

IR spectrum (CCl_4): 2945 (m), 1642 (w), 1449 (s), 1411 (m), 1362 (w), 1338 (w), 1246 (s), 1160 (m), 1078 (w), 1042 (s), 963 (s), 941 (m), and 854 (broad, s) cm^{-1}.

1,5-Bis(4′-trimethylsilyltetrafluorophenyl)pentane

To pentafluorophenyltrimethylsilane (5.1 g, 0.021 mole) in ether (50 ml) 1,5-dilithiopentane (20 ml, 0.58 M, 0.012 mole) was added in portions over 30 minutes while stirring at room temperature. Color Test I was negative after a further one hour. After addition of dilute hydrochloric acid, the ether layer was separated, dried ($MgSO_4$), and the ether evaporated. The residual green oil was distilled under reduced pressure (max. 180°C/1 mm) to give a colorless oil which slowly solidified to give a white solid (4.82 g, 88% crude yield) m.p. 62-64°C. Crystallisation from pentane gave a solid, m.p. 65.5-67.5°C, identified by infrared spectroscopy as 1,5-bis(4-trimethylsilyltetrafluorophenyl)-pentane.

IR spectrum (CCl_4): 2920 (m), 1640 (w), 1441 (s), 1406 (m), 1362 (w), 1256 (m), 1148 (w), 1102 (w), 1086 (m), 1045 (m), 934 (s) and 860 (broad, s) cm^{-1}.

1,6-Bis(4′-trimethylsilyltetrafluorophenyl)hexane

1,6-Dilithiohexane (0.0275 mole) in ether (100 ml) was added to trimethylpentafluorophenylsilane (13.2 g, 0.055 mole) in ether (50 ml) over one hour while stirring at 25°C. Color Test I was negative within ten hours. Work-up in the usual manner, followed by distillation under reduced pressure afforded: (i) a colorless liquid (0.85 g) containing by VPC two unidentified components; (ii) a very pale green oil which solidified on cooling (9.13 g, crude yield 63%), m.p. 65.5-66.5°C, which was identified as 1,6-bis(4′-trimethylsilyltetrafluorophenyl)hexane by infrared spectroscopy. Crystallisation from hexane afforded white crystals (5.13 g), m.p. 70.5-71°C.

IR spectrum (CCl_4): 2930 (m), 2850 (m), 1641 (w), 1440 (s), 1406 (m), 1361 (w), 1244 (s), 1142 (w), 1077 (w), 1041 (m), 988 (w), 916 (s), 862 (broad, s), and 846 (broad, s) cm^{-1}.

Preparation of Di-Grignard reagents from α,ω-dibromoalkanes

(a) From 1,4-dibromobutane

1,4-Dibromobutane (21.6 g, 0.1 mole) and magnesium turnings (13.5 g, 0.55 g atom) in THF (380 ml) were stirred until a vigorous reaction commenced, the reaction commenced, the reaction moderated by cooling to 15°C, and stirring continued at 15-20°C for 5 hr. Excess magnesium was filtered off and the concentration of the Grignard reagent determined by addition of an aliquot to excess acid and back titration with sodium carbonate. An 88% conversion to the di-Grignard reagent was indicated.

(b) From 1,5-dibromopentane

By a similar method, a di-Grignard reagent was obtained from 1,5-dibromopentane (23.0 g, 0.1 mole), magnesium (12.5 g, 0.51 g atom) and THF (250 ml). Titration as before indicated that a 0.335 M solution of the di-Grignard reagent was obtained, indicating 89% conversion.

1,5-Bis(trimethylsilyl)pentane

A solution of 1,5-dibromopentane (23.0 g, 0.10 mole) in THF (200 ml) was stirred with magnesium (12.5 g) at 20-25°C for 10 hr, filtered, and to it added chlorotrimethylsilane

(23.0 g, 0.215 mole)at 0°C. Color Test I was still positive after 15 minutes, and so the solution was stirred at room temperature until Color Test I was negative. Addition of dilute hydrochloric acid followed by work-up in the usual way afforded, on distillation, 1,5-bis(trimethylsilyl)-pentane (12.16 g, 53%), b.p. 105-108°C/10 mm (main fraction), n_D^{25} 1.4280 (cited[69] b.p. 216°C/760 mm n_D^{25} 1.4278), and also identified by infrared spectroscopy.[69]

In a similar experiment, the solution of the di-Grignard reagent in THF was kept for 12 hr at room temperature, followed by refluxing the solvent for 9 hr, and then again at room temperature for 3 hr, before adding chlorotrimethylsilane. 1,5-Bis(trimethylsilyl)pentane (12.51 g, 55%) was obtained, on distillation of the reaction product.

A small quantity of a residual colored oil could not be identified, but was present in both preparations. Analysis by VPC indicated that it contained at least three components.

Reaction of tetramethylenemagnesium bromide with hexafluorobenzene

Tetramethylenemagnesium bromide (0.047 mole) in THF (200 ml) was added to hexafluorobenzene (17.49 g). No reaction occurred at ambient temperature, and so the solution was refluxed for 45 hours, after which time Color Test I was finally negative. After addition of dilute hydrochloric acid the THF layer was separated and dried ($MgSO_4$). The solvent was removed by fractional distillation and the residue distilled under reduced pressure to give: (i) a colorless liquid (3.05 g), b.p. 70-75°C/28 mm, 80-84°C/35 mm, or 172-175°C, n_D^{20} 1.4261, and identified by infrared spectroscopy as n-butylpentafluorobenzene (cited,[45] b.p. 84-86°C/35 mm, 173-175°C/758 mm, n_D^{20}, 1.4229). Yield 29%; (ii) a mixture of fractions (i) and (iii), 0.35 g, b.p. 75-100°C/28mm; (iii) a colorless liquid (1.3 g), b.p. 100-130°C/28 mm, containing by VPC one unidentified compound; and, (iv) a liquid which solidified, m.p. 49.5-51°C and identified by infrared spectroscopy as slightly impure 1,4-bis(pentafluorophenyl)butane. Crude yield 2.91 g, 16%.

The residue from the distillation, 2.57 g, solidified on cooling and was not identified.

Reaction of pentamethylenemagnesium bromide with hexafluorobenzene

Pentamethylenemagnesium bromide (0.085 mole) in THF (255 ml) was added to hexafluorobenzene (37.2 g, 0.2 mole) in

THF (50 ml) and stirred at ambient temperature for 9 hours, after which time Color Test I was still positive. After refluxing the solution for 8 hours, Color Test I was negative. Work-up in the usual manner, followed by distillation under reduced pressure gave: (i) a colorless liquid (7.42 g), b.p. 100-120°C/28 mm. Analysis by VPC indicated that this liquid contained one major and two minor components; (ii) a pale green oil, b.p. 125-130°C/0.08 mm (1.5 g), unidentified; and (iii) some yellow unidentified solid at a high temperature. No 1,5-bis(pentafluorophenyl)pentane was isolated. Separation of fraction (i) by VPC (F and M "Prepmaster 776", silicone gum rubber/chromosorb) gave a 60% recovery of the three components. The minor components (0.21 g, and 1.01 g) remained unidentified, but the major component was identified as *n*-pentylpentafluorobenzene (3.27 g, 16%). Its infrared spectrum showed the presence of alkyl and polyfluorophenyl groups, and a correct molecular weight was obtained by mass spectroscopy.

IR spectrum (thin film): 2940 (m), 1730 (w), 1653 (w), 1520 (s), 1504 (s), 1470 (m), 1298 (w), 1194 (w), 1123 (s), 1077 (m), 1004 (m), 984 (m), 962 (s), 948 (s), 910 (w), and 727 (w) cm^{-1}. ($C_{11}H_{11}F_5$: mol. wt. 238.2. Found: 238.)

Reaction of pentafluorophenyllithium with 1,5-dibromopentane

(a) In ether

Pentafluorophenyllithium was prepared by addition of *n*-butyllithium (0.1 mole) in hexane (62.5 ml) to pentafluorobenzene (16.86 g, 0.1 mole) in ether (100 ml) at -70°C over 45 minutes. After stirring for a further 45 minutes, Color Test I was positive and Test II negative. 1,5-Dibromopentane (11.50 g, 0.05 mole) was added dropwise over 30 minutes while stirring. Color Test I was still positive after 34 hr at -70°C. The temperature was allowed to rise slowly at the approximate rate of 1.5°C per hour over 34 hours to -15°C. Color Test I was still positive but decomposition occurred at -10°C. The reaction mixture was worked up in the usual way. An intractable solid (3.5 g) was filtered off. Distillation of the residual liquid afforded 1,5-dibromopentane (9.26 g, 80%), b.p. 120-127°C/28 mm, identical to the starting material. The residue was a dark brown, viscous oil (14.5 g), and contained no 1,5-bis(pentafluorophenyl)pentane.

(b) In THF

n-Butyllithium (0.1 mole) in hexane (62.5 ml) was added to pentafluorobenzene (16.8 g, 0.1 mole) in THF (100 ml) at

-70°C dropwise over 45 minutes and the mixture stirred at this temperature for a further 30 minutes. 1,5-Dibromopentane (10.35 g, 0.09 mole) was added and after 10 hr at -70°C Color Test I was negative. The mixture was treated with dilute hydrochloric acid, filtered, the solvent layer separated and dried ($MgSO_4$). The dried solid (14.9 g) was not identified. Evaporation of the solvent followed by distillation of the residual liquid under reduced pressure afforded 1,5-dibromopentane (6.0 g, 58%) and a liquid (0.9 g, 3%) identified as 5-bromopentylpentafluorobenzene by infrared spectroscopy and molecular weight determination.

IR spectrum (thin film): 2935 (w), 1656 (w), 1525 (s), 1505 (s), 1460 (w), 1295 (w), 1120 (m), and 966 (s) cm^{-1}. ($C_{11}H_{10}BrF_5$: mol. wt. 317.2. Found: 317.)

(c) In mixed solvents

To n-butyllithium (0.05 mole) in hexane (31.5 ml), ether (31.5 ml) and THF (120 ml) at -70°C was added pentafluorobenzene (8.40 g, 0.05 mole) over 25 minutes, and the mixture stirred for a further 30 minutes at this temperature. Color Test II was negative and Test I positive after this time. 1,5-Dibromopentane (5.75 g, 0.05 mole) was added and the mixture stirred for 5 hr at -70°C, after which time Color Test I was still positive. The temperature was allowed to rise to -20°C over 15 hours, by which time Color Test I was negative. After addition of dilute hydrochloric acid, an infusible white solid (5.28 g) was filtered off. The solvent layer was dried ($MgSO_4$), the solvent evaporated, and the residual liquid distilled under reduced pressure to give 1,5-dibromopentane (3.06 g, 58%) and 5-bromopentylpentafluorobenzene (1.58 g, 10%). An intermediate fraction containing both components was separated into each component by VPC on an F and M "Prepmaster 776" at 150°C on silicone rubber/celite.

(d) In mixed solvents at -35° ± 10°C, in the presence of cobalt chloride

To pentafluorophenyllithium, prepared as before at -70°C in the same solvents from pentafluorobenzene (8.4 g, 0.05 mole), was added anhydrous cobalt chloride (0.63 g) followed by 1,5-dibromopentane (10.35 g, 0.045 mole) and the temperature raised from -70°C after 2.5 hours to -35° ± 10°C and held at this temperature for 15 hours, by which time Color Test I was negative. Work-up in the usual manner gave an infusible, unidentified, white solid (2.85 g) and a colorless liquid (6.62 g), b.p. 127-129°C/28 mm, n_D^{25} 1.5063. The liquid was identified as slightly impure 1,5-dibromopentane by infrared spectroscopy. No other products were isolated.

(e) In mixed solvents at -35° ± 10°C without cobalt chloride

With identical quantities as in (d) and under identical conditions the products were a white, infusible solid (3.5 g), 1,5-dibromopentane (3.76 g, 36%), and 5-bromopentylpentafluorobenzene (1.98 g, 12.5%), as identified by infrared spectroscopy.

Reaction of pentafluorophenyllithium with ethyl iodide

Pentafluorobenzene (8.43 g, 0.05 mole) was added to n-butyllithium (0.05 mole) in a mixture of hexane (31.5 ml), ether (31.5 ml) and THF (125 ml) at -70°C over 20 minutes. Within two hours, Color Test II was negative and Color Test I positive. Ethyl iodide (7.8 g, 0.05 mole) in pentane (5 ml) was added and the solution stirred at -70°C for 10 hours. Color Test I was still positive. The temperature was allowed to rise to 0°C at an average rate of 2.5-3°C/hr over a further 27 hours, by which time Color Test I was negative. After addition of dilute hydrochloric acid a white solid (1.66 g) was filtered off. The solvent layer was separated and the aqueous layer extracted with ether. The combined solutions were decolorized by shaking with aqueous sodium bisulphite and dried ($MgSO_4$). The solvents were fractionally distilled off and the residual liquid distilled on a Nester-Faust spinning band column. A colorless liquid, (4.02 g) b.p. 130-132°C, n_D^{23} 1.4085, n_D^{20} 1.4100, was obtained and identified as ethylpentafluorobenzene (cited[21] b.p. 132°C, n_D^{23} 1.4085). Re-distillation of lower boiling fractions afforded a total of 5.21 g, 53% yield of ethylpentafluorobenzene.

Reaction of pentafluorophenyllithium with 1,5-diiodopentane

Pentafluorophenyllithium was prepared by addition of pentafluorobenzene (8.43 g, 0.05 mole) to n-butyllithium (0.05 mole) in hexane (31.5 ml), THF (128 ml), and ether (32 ml) at -70°C over 30 minutes, and stirring at this temperature for 1.5 hours. 1,5-Diiodopentane (8.1 g, 0.025 mole) was added and the temperature raised to -35°C and held for 8 hours (Color Test I still positive), and then to -20°C for 10 hours by which time Color Test I was negative.

Work-up in the usual manner gave a white, infusible solid (2.19 g). Distillation of the solvent, and then the residual liquid under reduced pressure afforded a yellow liquid (2.14 g) containing many components by VPC, and a pale green liquid (5.27 g) which solidified, m.p. 49.5-51.5°C. Crystallisation of the latter from pentane gave white crystals (1.36 g), m.p. 55-56°C, and identified as 1,5-bis(pentafluorophenyl)pentane (mixed m.p. 56-56.5°C). Crude yield was 52%.

Reaction of pentafluorophenyllithium with diiodomethane

Pentafluorophenyllithium was prepared as before in the same solvents at -70°C from pentafluorobenzene (8.4 g, 0.05 mole). Diiodomethane (6.03 g, 0.0225 mole) was added and the mixture was kept at -70°C for 5 hours (Color Test I still positive) and then allowed to warm up to -20°C over 22 hours at an average rate of 2.5 minutes per hour. After this time, Color Test I was negative. Work-up as before gave a brown, infusible solid (1.86 g), and a small quantity of a pale yellow liquid (0.5 g), containing iodine. Decolorization with aqueous sodium bisulphite followed by redistillation afforded a few drops of a colorless liquid which gradually turned yellow in the light. This liquid was unidentified, but by VPC was not diiodomethane. Analysis of the last solvent fraction by VPC indicated that a component with a similar retention time to pentafluorobenzene was present.

Reaction of pentachlorophenyllithium with 1,6-dibromododecafluorohexane

Pentachlorophenyllithium was prepared by addition of *n*-butyllithium (0.022 mole) in hexane (14 ml) over 10 minutes to hexachlorobenzene (6.2 g, 0.022 mole) in THF (50 ml) at -70°C. After 1.75 hr at -70°C 1,6-dibromododecafluorohexane (4.5 g, 0.02 mole) in pentane (10 ml) was added and the mixture stirred at -70°C for 8.5 hours. Color Test I was negative within this time. All of the 1,6-dibromododecafluorohexane had been consumed as shown by analysis of an aliquot by GLC. The mixture was also seen to contain bromopentachlorobenzene and small quantities of pentachlorobenzene and hexachlorobenzene. The mixture was worked up in the usual manner. Evaporation of the solvent afforded a brown solid. Fractional sublimation gave a white solid which was crystallised from carbon tetrachloride to give white needles of bromopentachlorobenzene (3.02 g, 50%) m.p. 235.5°C (mixed m.p. 235-236°C, with an authentic sample kindly supplied by Dr. C. Tamborski).

Reaction of pentafluorophenyllithium with 1,6-dibromododecafluorohexane

To pentafluorophenyllithium, prepared by addition of *n*-butyllithium (0.012 mole) in hexane (7.5 ml) *via* a syringe to pentafluorobenzene (2.0 g, 0.012 mole) in THF (30 ml) and ether (7.5 ml) at -70°C, was added 1,6-dibromododecafluorohexane (2.75 g, 0.006 mole). After 4 hours at -70°C and then gradually warming to 0°C over 3 hours a white, infusible solid (1.0 g) was filtered off. Distillation after work-up in the usual manner afforded only 1,6-dibromododecafluorohexane (1.23 g, 44.5%) as identified by infrared spectroscopy. Distillation of the residues at 0.1 mm at an oil bath temperature of 250-280°C afforded a green oil (0.25 g) which solidified, but could not be identified.

Attempted preparation of 1,6-dilithiododecafluorohexane and reaction with hexafluorobenzene

To 1,6-dibromododecafluorohexane (5.0 g, 0.011 mole) in THF (50 ml) at -78°C was added 5 ml of a solution of *n*-butyllithium (0.022 mole) in pentane-hexane (40 ml) and then 5 ml of a solution of hexafluorobenzene (4.09 g, 0.022 mole) in THF (total volume 40 ml) after 5 minutes. This was repeated at 5 minute intervals by alternate addition of *n*-butyllithium and hexafluorobenzene until complete, and then more hexafluorobenzene (1.0 g). After a total of 2 hours at -78°C, the mixture was allowed to warm up to room temperature, and then worked up as before. The solvent was fractionally distilled off, but distillation of the brown residual liquid under reduced pressure afforded only a low boiling, pale yellow liquid (0.6 g) which by VPC contained only 1,6-dibromododecafluorohexane and another as yet unidentified component. Some tarry residues remained.

Attempted preparation of 1,2-bis(pentafluorophenyl)tetrachloroethane

n-Butyllithium (0.05 mole) in hexane (32 ml) was added over 50 minutes to 1,1,2,2-tetrachloroethane (4.2 g, 0.025 mole) in THF (128 ml), ether (32 ml) and pentane (15 ml) at -105° ± 2°C. After an additional 10 minutes, hexafluorobenzene (12.09 g, 0.065 mole) was added quickly and the mixture kept at -105° ± 2°C for 2 hours and then allowed to warm up to -80°C over 2 hours, and 0°C over a further 10 hours. Work-up in the usual manner, followed by fractional distillation of the solvent left a small quantity of a residual liquid. Further distillation gave only solvents containing hexafluorobenzene by VPC, and no tetrachloroethane or involatile residues.

Preparation of a pentafluorophenyllithium-TMEDA complex and attempted reaction with 1,5-dibromopentane

To *n*-butyllithium (0.1 mole) in pentane-hexane (360 ml) at 0°C was added TMEDA (15 ml), and the solution then cooled to -70°C. Pentafluorobenzene (16.8 g, 0.1 mole) was added over a period of 30 minutes and the solution stirred at -70°C for 1.5 hours. By this time Color Test II was negative (Test I positive). 1,5-Dibromopentane (10.35 g, 0.09 mole) was added and the solution stirred at -70°C for 5 hours. The temperature was allowed to rise at the average rate of 1.5-2°C per minute to -10°C over 40 hours, by which time Color Test I was negative. Work-up in the usual manner gave an infusible, white solid (15.15 g). Evaporation of the ether extract gave a gum (10.87 g) which could not be redissolved in ether, or boiling benzene, carbon tetrachloride, or xylene. No 5-bromopentylpentafluorobenzene or 1,5-bis(pentafluorophenyl)pentane was detected by VPC or by attempted extraction of the gum with ether.

IX. PREPARATION OF SOME SILYL-SUBSTITUTED POLYHALOARYLPHOSPHINES

A. INTRODUCTION

The preparation of tertiary phosphines by the reaction of Grignard reagents or aryllithium compounds with phosphorous halides (including alkyl and aryl) is well known and has been reviewed.[91] Quite recently interest has been shown in the synthesis and properties of tertiary phosphines with polyhalophenyl groups on phosphorus.[59b,22] However, silyl-substituted polyhaloarylphosphines are not known. We now report the preparation of bis(silyl-substituted polyhaloaryl)-phenylphosphines, in connection with our studies concerned with thermally stable compounds and monomers which could give rise to useful, thermally stable polymers.

B. RESULTS AND DISCUSSION

As a part of the investigation into the preparation of silyl-substituted polyhaloaryl phosphines, we wished to synthesize bis(4-trimethylsilyltetrachlorophenyl)phenylphosphine (I) and bis(4-trimethylsilyltetrafluorophenyl)-phenylphosphine (II). The synthesis of (I) has been achieved by the following two different routes:

$$\text{(i)}\quad C_6Cl_5SiMe_3 \xrightarrow[\text{THF}]{\underline{n}\text{-BuLi}} \xrightarrow{C_6H_5PCl_2} (Me_3SiC_6Cl_4)_2PC_6H_5$$

(I)

$$\text{(ii)}\quad (C_6Cl_5)_2PC_6H_5 \xrightarrow[\text{THF}]{\underline{n}\text{-BuLi}} \xrightarrow{Me_3SiCl} (Me_3SiC_6Cl_4)_2PC_6H_5$$

Both the compounds were found to be identical from their infrared spectra and mixed melting point. The lithiation of trimethylsilylpentachlorobenzene with n-BuLi is reported[50] to take place at the 4-position. Based on this report, (I) is assigned as bis(4-trimethylsilyltetrachlorophenyl)phenylphosphine.

The poor yield of (I) in (i) could be due to C-Si bond breaking by n-BuLi,[87] giving rise to a dianion which would give a polymeric material by reaction with a difunctional compound, like $C_6H_5PCl_2$. A similar observation is encountered in the preparation of bis(4-trimethylsilyltetrafluorophenyl)-phenylphosphine from 1-trimethylsilyl-2,3,5,6-tetrafluorobenzene via the route (i), resulting in only a 10% yield of the desired compound. Such a side reaction is, probably, not favored in (ii) and the yields by this method are reasonable.

C. EXPERIMENTAL

All reactions were carried out under dry oxygen-free nitrogen atmosphere. Glassware used in these experiments was dried in oven at 130°C, assembled while hot and flushed with nitrogen. Tetrahydrofuran was ketyl purified and was distilled directly into the reaction vessel. IR and UV spectra were recorded employing, respectively, a PE-21 infrared spectrometer and a Cary-14R spectrometer. All melting points and boiling points are uncorrected.

Reaction of pentachlorophenylmagnesium chloride with phenyldichlorophosphine

The Grignard reagent was prepared in the usual manner[60] from 28.5 g (0.1 mole) of hexachlorobenzene and 9.6 g (0.4 g atom) of magnesium in 150 ml of dry tetrahydrofuran; filtered; and was added dropwise with stirring at room temperature to 9.0 g (0.05 mole) of phenyldichlorophosphine in 20 ml of THF. The mixture was stirred for about six hours and poured into 10% ice-cold hydrochloric acid. The organic layer was extracted with ether, dried ($MgSO_4$) and the solvent was distilled off under reduced pressure to give a dark brown solid. The solid was taken up in carbon tetrachloride and chromatographed on neutral alumina. Removal of the solvent and crystallisation from carbon tetrachloride gave a pale yellow solid (6 g, 20%), m.p. 238-240°C. ($C_{18}H_5Cl_{10}P$ calcd.: mol. wt. 607. Found: mol. wt. 607 (mass spec.))

Pentachlorophenyllithium and phenyldichlorophosphine

To pentachlorophenyllithium in THF, prepared by a reported procedure[59b] from hexachlorobenzene (14.3 g, 0.05 mole) and n-BuLi (33 ml, 0.05 mole) at -78°C, was added 4.5 g (0.025 mole) of phenyldichlorophosphine in 20 ml of THF.

Color Test I was positive after stirring for 48 hours at -78°C. The temperature was raised to -20°C during the next 24 hours after which Color Test I was negative. The solvent was vacuum removed and the residue was extracted with hot benzene. Removal of benzene and crystallisation of the solid from carbon tetrachloride gave 7.2 g (47%), based on the formation of $(C_6Cl_5)_2PC_6H_5$, m.p. 238-240°C. Mixed melting point with the sample from the previous reaction was undepressed. The IR spectra of both samples were superimposable.

Oxidation of bis(pentachlorophenyl)phenylphosphine to phosphine oxide

The oxidation was carried out by a procedure reported by Wall *et al.*[22] Bis(pentachlorophenyl)phenylphosphine (2 g, 0.0033 mole) was placed in a solution of 15 g of $Na_2Cr_2O_7$, in 25 ml of water, acidified with 15 ml of concentrated sulphuric acid and 25 ml of glacial acetic acid. The mixture was refluxed for ten hours, neutralised with $NaHCO_3$ solution and extracted with 3 x 50 ml portions of chloroform. The chloroform solution was dried ($MgSO_4$) and the solvent was removed under vacuum to give 1.7 g (84%) of bis(pentachlorophenyl)phenylphosphine oxide, m.p. 246-248°C after crystallisation from Skelly B.

Reaction of bis(pentachlorophenyl)phenylphosphine with n-BuLi and subsequent treatment with trimethylchlorosilane

To 5 ml (0.0072 mole) of *n*-BuLi in 20 ml of THF at -78°C was added a THF solution of bis(pentachlorophenyl)-phenylphosphine (2.2 g, 0.0036 mole) in 10 ml of THF, with stirring. After about 30 minutes, Color Test II was negative and I positive. Trimethylchlorosilane (4 g) in 5 ml of THF was added dropwise and stirred until Color Test I was negative (ca. 30 minutes). The solvent and unreacted trimethylchlorosilane were vacuum removed. The residue was taken up in water and extracted with ether. The ether extract was dried ($MgSO_4$) and the solvent was removed at pump to give 1.7 g (75%) of a solid which after crystallisation from methanol melted at 74-75°C.

Trimethylsilylpentachlorobenzene, n-butyllithium and phenyldichlorophosphine

Trimethylsilylpentachlorobenzene, m.p. 116°C, was prepared in 60% yield from hexachlorobenzene, *n*-butyllithium and trimethylchlorosilane.[59b] To 35 ml (0.05 mole) of *n*-butyllithium in 100 ml of THF at -78°C was added a THF solution of 16.0 g (0.05 mole) of trimethylsilylpentachlorobenzene, with stirring over one hour, after which Color Test

II was negative and I positive. Phenyldichlorophosphine (4.5 g, 0.025 mole) in 10 ml of THF was added dropwise and stirred. Color Test I was negative after 30 minutes. The solvent was stripped off in vacuum and the residue was taken up in 100 ml of 5% sodium hydroxide solution and extracted with ether. The ether extract was dried ($MgSO_4$) to give a thick viscous oil which was chromatographed on alumina, employing Skelly B as eluent. Removal of solvent gave a pale yellow solid, 7.0 g (42%), m.p. 74-75°C after crystallisation from methanol. The infrared spectrum of this compound was found to be identical with that of the compound obtained in the previous reaction.

Reaction of pentafluorophenylmagnesium bromide with phenyldichlorophosphine

To 0.1 mole of pentafluorophenylmagnesium bromide [prepared from 24.7 g (0.1 mole) of bromopentafluorobenzene and 2.6 g (0.11 g atom) of magnesium in 150 ml ether] was added 9.0 g (0.05 mole) of phenyldichlorophosphine in 20 ml ether at room temperature and refluxed for an additional six hours. The reaction mixture was decomposed with cold dilute hydrochloric acid, extracted with ether and dried. The solvent was removed under vacuum to give a thick viscous dark brown liquid which was distilled employing a spinning band column. A thick colorless liquid, 9.3 g (48%), b.p. 115-117°C/0.1 mm (n_D^{20} 1.4570), was obtained which solidified after keeping for 24 hours. The solid melted at 62°C after crystallisation from methanol. ($C_{18}H_5F_{10}P$ calcd.: mol. wt. 442. Found: mol. wt. 442 (mass spec))

Oxidation of bis(pentafluorophenyl)phenylphosphine to its oxide

Bis(pentafluorophenyl)phenylphosphine, 2.3 g (0.0052 mole) in sodium dichromate solution (20 g of $Na_2Cr_2O_7$, in 25 ml of water) was acidified with a mixture of 50 ml of glacial acetic acid and 20 ml of concentrated sulphuric acid and refluxed for eight hours. The mixture was neutralised with $NaHCO_3$ solution and extracted with 3 x 50 ml portions of chloroform. The extract was dried ($MgSO_4$) and the solvent removed under vacuum to give 1.1 g (46%) of bis(pentafluorophenyl)phenylphosphine oxide, m.p. 102-103°C after crystallisation from Skelly B.

1-Trimethylsilyl-2,3,5,6-tetrafluorobenzene, n-butyllithium and phenyldichlorophosphine

1-Trimethylsilyl-2,3,5,6-tetrafluorobenzene (b.p. 82-84°C/43 mm; n_D^{20} 1.4450) was prepared in 55% yield from

1,2,4,5-tetrafluorobenzene, n-butyllithium and trimethylchlorosilane, by a standard procedure.[93] To n-butyllithium (35 ml, 0.05 mole) in 50 ml of THF at -78°C was added a THF solution of 11.1 g (0.05 mole) of 1-trimethylsilyl-2,3,5,6-tetrafluorobenzene in 10 ml of THF, with stirring over a 30 minute period, after which Color Test II was negative and Test I positive. Phenyldichlorophosphine (4.5 g, 0.025 mole) in 5 ml of THF was added dropwise and stirred until Color Test I was negative (ca. 1 hour). The solvent was removed, the residue was washed with 5% sodium hydroxide solution and taken up in ether. The ether extract was dried and the solvent was removed under vacuum to give a pale yellow thick viscous liquid which refused to solidify even after keeping for twenty hours at dry ice temperature. The oil was finally fractionally distilled to give a colorless liquid, b.p. 48°C/0.01 mm, which deposited a crystalline solid [1.3 g, 9.4% based on the formation of bis(trimethylsilyltetrafluorophenyl)phenylphosphine], m.p. 52-53°C after crystallisation from pentane.

Reaction of 1,2,4,5-tetrafluorobenzene with n-butyllithium followed by treatment with phenyldichlorophosphine

A THF solution of 1,2,4,5-tetrafluorobenzene (30 g, 0.2 mole) was added to n-butyllithium (125 ml, 0.2 mole) in 150 ml of THF at -78°C, with stirring. After one hour, Color Test II was negative and Test I positive. Phenyldichlorophosphine (18 g, 0.1 mole) in 50 ml of THF was added dropwise and stirred for sometime until Color Test I was negative. The solvent was removed under vacuum, and the residue was taken up in ether and washed with 5% caustic soda solution. The ether extract was dried ($MgSO_4$) and the solvent was removed at pump to give 22 g (55%) of solid, m.p. 85-86°C after crystallisation from pentane.

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13. ABSTRACT

The primary objective of our studies is the preparation of useful, thermally stable fluids, lubricants, etc. This has involved the synthesis of compounds containing units having particularly a plurality of fluorine atoms, as well as some having a plurality of chlorine atoms. These as well as the silicon atoms contained in many of the compounds should provide monomers having reactive functional groupings to give access to novel thermally stable polymers. Among the polyfluoro types being studied are those containing a bridge such as $-(CF_2)_n-$.

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