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PENTACHLOROPHENYL DERIVATIVES OF SILICON AND TIN

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Since the preparations of pentafluorophenylmagnesium bromide and iodide[1] and pentafluorophenyllithium[2] were reported, there have been many investigations conducted on the syntheses and properties of compounds of Group IVB elements which contained one or more pentafluorophenyl groups directly bonded to the metal atoms[3-10].

We now wish to report the preparations of some compounds containing pentachlorophenyl groups directly bonded to a silicon or tin atom.

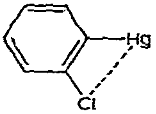
Pentachlorophenylmagnesium chloride was first reported in 1959 by Rosenberg and co-workers[11-13], and it was prepared by the interaction of a four-fold excess of magnesium turnings with hexachlorobenzene in tetrahydrofuran, using a small crystal of iodine and ethyl bromide to initiate the reaction. The yield of the Grignard reagent, as determined by hydrolysis to pentachlorobenzene, was 60.0%. Pearson and co-workers[14,15] were able to prepare the Grignard reagent in diethyl ether by a modified entrainment method using ethylene bromide instead of ethyl bromide used by the previous authors[11-13]. The yield, as determined by carbonation, followed by hydrolysis to give pentachlorobenzoic acid was 71%.

The lithium reagent, pentachlorophenyllithium, was reported recently by Rausch and co-workers[16]. It was made by halogen–metal interconversion between hexachlorobenzene in either diethyl ether or tetrahydrofuran, with commercial n-butyllithium in hexane. The lithium reagent was characterized by forming pentachlorophenyl derivatives of Hg, Si, P, Co, Ni and other elements. Carbonation and hydrolysis lead to pentachlorobenzoic acid and pentachlorobenzene, respectively.

The same intermediate, pentachlorophenyllithium, can also be prepared by metalating[17] pentachlorobenzene with n-butyllithium at −60°. Extensive hydrogen–lithium exchange to give pentachlorophenyllithium was observed, giving, after carbonation and hydrolysis, 91% of pentachlorobenzoic acid. Small amounts of products due to chlorine–lithium interconversion were also obtained.

Recently, the reaction of pentachlorophenylmagnesium chloride with mercuric chloride to form bis(pentachlorophenyl)mercury was reported[18]. Mono-substituted pentachlorophenylmercury compounds could be made by prolonged heating at temperatures above 200° of bis(pentachlorophenyl)mercury with another organomercury compound. The following pentachlorophenyl derivatives of mercury have been prepared: $(C_6Cl_5)_2Hg$, C_6Cl_5HgCl, $C_6Cl_5HgCH_3$ and $C_6Cl_5HgC_6H_5$. The same authors found that these compounds have very high thermal stabilities. When attacked by acid, the ease of cleavage from mercury is in the following order: $C_6H_5 >$

$C_6Cl_5 > CH_3$. The authors also suggested possible interaction between mercury and the ring halogen atoms.



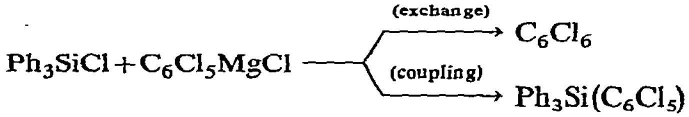
The only compound which contains a pentachlorophenylsilicon σ-bond mentioned in the literature up to the present is (pentachlorophenyl)trichlorosilane. This compound is prepared by the chlorination of phenyltrichlorosilane in the presence of a catalyst (Fe and $AlCl_3$, or I_2 and $SbCl_3$)[19]. By using different temperatures

$$(C_6H_5)SiCl_3 + Cl_2 \xrightarrow{\text{Fe and AlCl}_3} (C_6Cl_5)SiCl_3$$

and reagent ratios, it is possible to isolate the entire series from the mono- to pentachlorophenyl derivatives. Attempts made by the same authors to prepare bis(pentachlorophenyl)dichlorosilane by the chlorination of diphenyldichlorosilane have not been successful[19].

In our preparation of pentachlorophenylmagnesium chloride, a few drops of ethylene bromide were used to initiate the reaction between hexachlorobenzene and magnesium in tetrahydrofuran. When an acid-hydrolyzed aliquot of the Grignard reagent was analyzed by vapor phase chromatography, the chromatogram showed a small band, followed by a relatively large band. These bands correspond to those obtained from authentic samples of 1,2,4,5-tetrachlorobenzene and pentachlorobenzene, respectively. The total base titration of a 2 ml aliquot from a customary preparation gave a yield of 105%. These observations may suggest that about 5% of the reaction mixture is the di-Grignard reagent and 95% of the reaction mixture is the mono-Grignard reagent. Pentachlorophenylmagnesium chloride can also be prepared in low yield by halogen–metal exchange between hexachlorobenzene and benzylmagnesium chloride in a mixture of diethyl ether and THF as solvent. In reactions of hexachlorobenzene with metals such as lithium or magnesium there probably are also formed benzynes and dibenzynes as well as radical-anions.

Pentachlorophenylmagnesium chloride reacts with a triarylchlorosilane to give mainly a coupling product, with very little of the exchange product.



$$Ph_3SiCl + C_6Cl_5MgCl \; \begin{array}{l} \xrightarrow{\text{(exchange)}} C_6Cl_6 \\ \xrightarrow{\text{(coupling)}} Ph_3Si(C_6Cl_5) \end{array}$$

However, if a polychlorosilane is used, the chlorine–magnesium chloride exchange reaction becomes important. In the reaction between pentachlorophenylmagnesium chloride and phenyltrichlorosilane, the only products isolated were hexachlorobenzene, and some dark brown tar. No coupling product, tris(pentachlorophenyl)phenylsilane, has as yet been isolated from this reaction. It is not certain at this stage whether steric hindrance is a significant factor in the unsuccessful preparation of tris(pentachlorophenyl)phenylsilane.

Several attempts have also been made to prepare tetrakis(pentachlorophenyl)silane by treating pentachlorophenylmagnesium chloride with silicon tetrachloride;

however, the main product isolated was hexachlorobenzene, resulting from chlorine–magnesium chloride exchange. In one of these attempts, tetrakis(pentachlorophenyl)silane, m.p. 402–403°, was obtained. Silicon analysis of the product was made and the results agreed quite well with the calculated value for tetrakis(pentachlorophenyl)silane. In order to reduce the halogen–metal exchange reaction, pentachlorophenylmagnesium chloride was treated with tetraethoxysilane instead of silicon tetrachloride; however, no tetrakis(pentachlorophenyl)silane was isolated. A reaction between pentachlorophenyllithium and silicon tetrachloride was also attempted; however, no compound melting at 402–403° was isolated. Instead hexachlorobenzene and a small amount of pentachlorobenzene were isolated. (See footnote *a* in Table 1.)

Similar results have been observed in the reaction between pentachlorophenylmagnesium chloride and tin tetrachloride, *i.e.* the exchange product becomes predominant as the number of chlorine atoms in the tin compound increases.

Some of the pentachlorophenyl derivatives of silicon or tin which were prepared from pentachlorophenylmagnesium chloride and the corresponding chlorosilane or tin chloride are listed in Table 1.

TABLE 1

PENTACHLOROPHENYL DERIVATIVES OF Si OR Sn

Compound	*M.p.*	*Yield* (%)	*Si or Sn cont.*		*Mol. weight*	
			Calcd.	*Found*	*Calcd.*	*Found*
$Ph_3SiC_6Cl_5$	217–220°	50%	5.51	5.67	508	518
$Ph_2Si(C_6Cl_5)_2$	239–240°	35.8%	4.13	4.00 3.94	681	687
$Si(C_6Cl_5)_4$	402–404°	~3%	2.73	2.69 3.19	1026	[a]
$Ph_3SnC_6Cl_5$	170–172°	67.3%	19.82	19.80 20.18	599	580
$Ph_2Sn(C_6Cl_5)_2$	237–240°	39.2%	15.25	14.95 14.88	772	841
$Sn(C_6Cl_5)_4$	446–449° (decomp.)	3.9%	10.62	10.76 10.50	1106	1100 ± 10[b]

[a] The compound was too insoluble to allow determination of its molecular weight osmometrically in benzene. The value of 954 obtained from the mass spectrum indicates that the compound has two chlorine atoms less than the required number. [b] The mass spectrum shows the molecular ion at 1100 ± 10. This uncertainty is due to loss of resolution and sensitivity at the very upper limit of the spectrometer's usability. Confirmatory evidence of this molecular weight is obtained from the intense ion cluster centered at 854 due to the expected loss of a pentachlorophenyl fragment.

The ultraviolet properties of these compounds were studied, and all of them showed absorption maxima at about 220 $m\mu$ with extraordinarily high molar absorptivities. It was also observed that these molar absorptivities increased with the number of pentachlorophenyl groups. Furthermore, the tin compounds have higher molar absorptivities than those of the analogous silicon compounds. At this time, the following is a possible interpretation of these unusual results: the ability of empty *d*-orbitals of silicon and tin to interact with (*i*) the π-electrons of a phenyl or pentachlorophenyl ring, or (*ii*) the unshared electron pairs of the ortho chlorine atoms,

TABLE 2

UV SPECTRAL DATA OF SOME PENTACHLOROPHENYL DERIVATIVES

Compound	*Band position*[a] $\lambda_{max}(m\mu)$	*Molar absorptivity*
$Ph_3SiC_6Cl_5$	218	64,930
$Ph_2Si(C_6Cl_5)_2$	221	100,000
$Si(C_6Cl_5)_4$	220	134,000
$Ph_3Sn(C_6Cl_5)$	218	85,830
$Ph_2Sn(C_6Cl_5)_2$	219	116,900
$Sn(C_6Cl_5)_4$[b]		

[a] The solvent used was cyclohexane. [b] The compound was insoluble in cyclohexane.

forming pentacoordinated or hexacoordinated silicon or tin atoms. The ultraviolet properties of these compounds are listed in Table 2.

Some reactions of these pentachlorophenyl derivatives will be reported in a subsequent paper.

The ultraviolet spectra of tetraphenylsilane and tetraphenyltin were previously determined by Freedman[20] and by Griffiths[21], respectively. In 95% ethanol, tetraphenylsilane absorbs at 203.5 mμ, 254 mμ, 260 mμ and 264.5 mμ (ε 48,000, 1480, 1590 and 1450, resp.) The ultraviolet spectrum of this compound was also reported by Milazzo[22] and LaPaglia[23]. In cyclohexane, tetraphenyltin absorbs at 210 mμ, 257 mμ, 282 mμ, 291 mμ and 298 mμ (ε 50,000, 1250, 31.6, 20 and 8, resp.).

EXPERIMENTAL

All melting points are uncorrected and were obtained using a Mel-Temp apparatus. Hexachlorobenzene and magnesium turnings were obtained commercially in reagent grade. Tetrahydrofuran was dried over sodium wire before use. Reactions involving organometallic compounds were carried out under an atmosphere of dry, oxygen-free nitrogen. All apparatus was dried in an oven at 110° before use. Ultraviolet spectra were determined using a Beckman DK-2A Spectrophotometer. Vapor phase chromotographic analyses were made with an F and M Model 500 Gas Chromatograph, using a column packed with silicon gum rubber SE30 on Chromosorb W (1 : 20). Molecular weight determinations were made with a Mechrolab Model 301-A Vapor Pressure Osmometer. Benzil was used as a standard with benzene as solvent.

Preparation of pentachlorophenylmagnesium chloride

(*a*) *From hexachlorobenzene and magnesium.* A 250-ml three-necked flask was equipped with a mechanical stirrer, a condenser and an addition funnel. Into the flask, 3.6 g (0.15 g-atom, 50% excess) of magnesium turnings which had been dried in a 100° oven and about 6 drops of dry ethylene bromide, were introduced. From the addition funnel, a small amount of a slurry which contained 28.5 g (0.1 mole) of hexachlorobenzene and 120 ml of sodium-dried tetrahydrofuran was added to the reaction mixture. Stirring was started, and after about 5 minutes the reaction set in as indicated by the evolution of heat and the appearance of a dark brown color.

The rest of the hexachlorobenzene/tetrahydrofuran slurry was added in small portions to maintain the reaction mixture under slow reflux. After the addition of the slurry the mixture was stirred at room temperature for three or more hours to complete the reaction. The Grignard solution was then filtered through glass wool into an addition funnel in order to remove any unchanged magnesium. It gave a weakly positive Color Test I[24]. Several 2 ml aliquots of this solution were hydrolyzed and the total base contents were determined by titration with standard acid to give yields ranging from 98 to 105%. VPC analysis of an hydrolyzed aliquot indicated the mono- and *p*-di-Grignard reagents in the ratio of about 20:1.

(*b*) *From hexachlorobenzene and benzylmagnesium chloride.* Benzylmagnesium chloride (0.25 mole) was prepared by treating 31.6 g (0.25 mole) of benzyl chloride with an excess of magnesium in 120 ml of diethyl ether. A total base titration showed a 95.2% yield of the Grignard reagent. Hexachlorobenzene (28.5 g, 0.1 mole) and THF (100 ml) were placed in a 250 ml flask. The mixture was stirred and 75 ml of diethyl ether solution containing 0.1 mole of benzylmagnesium chloride was added over 2 minutes. The reaction was very exothermic, and the color of the reaction mixture was dark brown. Thirty minutes after the addition of benzylmagnesium chloride, Color Test I[24] of the reaction mixture was negative. The reaction mixture was carbonated by pouring it into a slurry of Dry Ice in ether. The work-up gave 2.0 g (6.8%) of pentachlorobenzoic acid, m.p. and mixed m.p. 204–206°. A small amount of 2,3,5,6-tetrachlorobenzenedicarboxylic acid, m.p. 340–342° (decomp.) was also obtained. The reported m.p. of 2,3,5,6-tetrachlorobenzenedicarboxylic acid is 343–345° (decomp.)[25]. However, the major product was polymeric brownish material which melted between 340–345°.

Preparation of (pentachlorophenyl)triphenylsilane

Pentachlorophenylmagnesium chloride (0.1 mole) in 100 ml THF was added dropwise to a solution which contained 29.5 g (0.1 mole) of triphenylchlorosilane. The addition was completed within 30 minutes and heat was evolved during this time. The reaction mixture was stirred overnight at room temperature and then for two hours at the reflux temperature. When cool, it was hydrolyzed with 200 ml of aqueous ammonium chloride solution. The precipitate formed was separated by filtration, and the organic fraction of the filtrate was separated from the aqueous fraction. The organic fraction was dried over sodium sulfate and then concentrated to give a solid residue. Petroleum ether (b.p. 60–70°) was added to the combined solid materials and the mixture was heated to the reflux temperature, dissolving the small amount of hexachlorobenzene. The insoluble materials were separated by filtration, and then recrystallized from benzene to give 27.55 g (50.5%) of (pentachlorophenyl)triphenylsilane, m.p. 217–220°. The ultraviolet spectrum of (pentachlorophenyl)triphenylsilane in cyclohexane gave λ_{max} 218 mμ (ε 64,930), 297 mμ (ε 1040), 307 mμ (ε 1250). [Found: Si, 5.67, 5.47; mol.wt. (vapor pressure osmometer), 518. $C_{24}H_{15}Cl_5Si$ calcd.: Si, 5.51%; mol.wt., 508.6.]

A second preparation of the compound was carried out in which the manner of addition was reversed, *i.e.* dropwise addition of triphenylchlorosilane to the Grignard reagent. The reaction mixture was worked up in the same manner as the first preparation to give a 70% yield of (pentachlorophenyl)triphenylsilane. The compound was identified by mixed m.p. with an authentic sample.

Preparation of bis(pentachlorophenyl)diphenylsilane

A solution of 0.1 mole pentachlorophenylmagnesium chloride in 100 ml of THF was added dropwise to 10.13 g (0.04 mole) of diphenyldichlorosilane in 30 ml of THF. Heat was evolved during the addition and solid particles precipitated out during the stirring period. After the reaction mixture had been stirred overnight at room temperature it was refluxed for 1 h to ensure completion of the reaction. The suspension was hydrolyzed with aqueous ammonium chloride and the insoluble materials were separated by filtration. The organic fraction of the filtrate was separated from the aqueous fraction and dried over sodium sulfate. The organic solvents were removed on a rotary evaporator and a black oil remained. Upon addition of petroleum ether (b.p. 60–70°) to the black oil, solids were formed which showed signs of melting at about 100°, and at about 200° white solids sublimed onto the inner walls of the capillary tube. At about 210°, melting of the solids occurred. This behavior suggested the presence of hexachlorobenzene and pentachlorobenzene. The insoluble materials separated by filtration at the beginning also showed the same melting point behavior. All the solids isolated from the reaction were combined and recrystallized from benzene, using Norit-A to remove the black color. Upon concentration, solids were obtained. Petroleum ether (b.p. 60–70°) was added and the whole boiled to dissolve the hexachlorobenzene and pentachlorobenzene. The insoluble material was separated and redissolved in benzene. After two recrystallizations from benzene, the compound melted constantly at 239–240°. The total yield was 10.5 g (38.5%) of bis(pentachlorophenyl)diphenylsilane. The ultraviolet spectrum in cyclohexane gave λ_{max} 221 mμ (ε 100,000), 297 mμ (ε 1516), 308 mμ (ε 1842). The infrared spectrum (in CS_2) contained absorptions in μ at: 3.4, 7.7, 8.6, 9.15 and 11.6. [Found: Si, 4.00, 3.94; mol.wt. (vapor pressure osmometer), 687. $C_{24}H_{10}Cl_{10}Si$ calcd.: Si, 4.13%; mol.wt., 681.]

Preparation of tris(pentachlorophenyl)phenylsilane (attempted)

A 0.1 mole pentachlorophenylmagnesium chloride solution in 100 ml of THF was added dropwise to 5.72 g (0.027 mole) of phenyltrichlorosilane in 20 ml of THF. The reaction mixture was stirred for several hours at room temperature and then for 3 h at the reflux temperature. The solution was hydrolyzed with aqueous ammonium chloride and the organic fraction was separated from the aqueous fraction. After drying the organic fraction over sodium sulfate, it was distilled to remove the organic solvents. The black, polymeric residue was chromatographed on activated alumina, using a mixture of petroleum ether (b.p. 60–70°) and benzene as eluent, to give only hexachlorobenzene, m.p. 224–226°. The compound was identified by mixed m.p. with an authentic sample. The other product was a polymeric oil which failed to give any crystalline material in several different organic solvents.

A second attempt to prepare tris(pentachlorophenyl)phenylsilane was made, but, only hexachlorobenzene was isolated and identified by mixed m.p. with an authentic sample. All attempts to isolate any crystalline compound from the black, polymeric residue were unsuccessful.

A third attempt was then made to prepare tris(pentachlorophenyl)-phenylsilane by the treatment of 5.3 g (0.025 mole) of phenyl trichlorosilane in 30 ml of THF with 0.1 mole of pentachlorophenyllithium. The pentachlorophenyllithium was prepared by treating 28.5 g (0.1 mole) of hexachlorobenzene in 120 ml of THF with

0.1 mole of n-butyllithium in 66 ml of diethyl ether at −50° in a Dry Ice/acetone bath. Within 10 minutes of the addition of n-butyllithium Color Test II[26] was negative indicating the consumption of n-butyllithium. Color Test I was positive. One hour after the addition of pentachlorophenyllithium to phenyltrichlorosilane, Color Test I was negative. The reaction mixture was worked up anhydrously by removing the organic solvents (THF and diethyl ether) on a rotary evaporator, leaving behind a black oil. Sodium-dried benzene was added to dissolve the organic material and the insoluble magnesium chloride was separated by filtration. The benzene filtrate was concentrated and a black oil obtained. Petroleum ether (b.p. 60–70°) was added to solidify the black oil. The resultant light brown solid had no definite m.p. and part of it sublimed on the walls of the capillary tube at about 160°. These solids were then sublimed to give 4.2 g of white hexachlorobenzene, m.p. 226–228°, which was identified by mixed m.p. with an authentic sample. The remaining 9.3 g of light brown solid which softened at 100° and had no definite m.p., was dissolved in benzene to give an oil. No further attempts were made to identify this oil.

Reaction between pentachlorophenylmagnesium chloride and silicon tetrachloride

A 0.1 mole of pentachlorophenylmagnesium chloride solution in 100 ml of THF was added dropwise to 4.25 g (0.025 mole) of silicon tetrachloride in 25 ml of THF. During the addition a white solid precipitated out which was identified by mixed m.p. as hexachlorobenzene. The reaction mixture was stirred for three hours at room temperature and then for two hours at the reflux temperature. It was worked up anhydrously by removing the organic solvent on a rotary evaporator, and 35 g of a mixture of magnesium chloride, hexachlorobenzene and some coupling products were obtained. Benzene was added to these solids and the mixture was boiled to dissolve the hexachlorobenzene. The insoluble material was separated by filtration and the benzene filtrate, upon concentration, gave 4.0 g (14.5%) of hexachlorobenzene, m.p. 226–228°, which was identified by mixed m.p. with an authentic sample. The insoluble material was boiled with xylene and filtered. The xylene filtrate, upon concentration, gave a small amount of solid melting at 380–386°. This was recrystallized from benzene several times until the constant m.p. 402–404° was obtained. The weight of the pure compound obtained was 0.77 g (3%, based on tetrakis(pentachlorophenyl)silane.) The ultraviolet spectrum in cyclohexane gave λ_{max} 220 mμ (ε 134,000), 305 mμ (ε 12,100), 314 mμ (ε 13,859). The infrared spectrum (in CS_2) contained absorptions in μ at: 3.3, 7.75, 8.6, 8.7, 9.0, 9.15 and 11.45. [Found: Si, 2.73, 3.19; mol.wt. (mass spectrum), 954. $C_{24}Cl_{20}Si$ calcd.: Si, 2.69%; mol.wt., 1026.]

Preparation of (pentachlorophenyl)triphenyltin

A 0.05 mole pentachlorophenylmagnesium chloride solution in 80 ml of THF was added slowly to 19.3 g (0.05 mole) of triphenyltin chloride in 30 ml of THF. The reaction mixture warmed slightly during the addition. The solution was stirred overnight at room temperature and then for 2 h at the reflux temperature. It was hydrolyzed with aqueous ammonium chloride solution. The organic fraction was separated and dried over sodium sulfate. Removal of the organic solvents on a rotary evaporator gave 24.25 g of solids melting over the range of 180–190°. Petroleum ether (b.p. 60–70°) was added to these solids and the mixture was boiled to remove the hexachlorobenzene which was formed in the reaction. The less soluble material was separated by filtration. The petroleum ether filtrate was concentrated to give 3.1 g (21.8%) of hexachlorobenzene melting at 225–228° and identified by mixed m.p. with an authentic sample. The less soluble material was recrystallized from benzene several times until a constant m.p. 170–172° was attained. The yield was 20.1 g (67.3%) of (pentachlorophenyl)triphenyltin. The ultraviolet spectrum in cyclohexane gave λ_{max} 218 mμ (ε 85,830), 292 mμ (ε 8150) and 307.5 mμ (ε 8150). [Found: Sn, 19.80, 20.20; mol.wt. (vapor pressure osmometer), 582. $C_{24}H_{15}Cl_5Sn$ calcd.: Sn, 19.82%; mol.wt., 599.]

Preparation of bis(pentachlorophenyl)diphenyltin

Pentachlorophenylmagnesium chloride (0.1 mole) in 100 ml of THF was added dropwise to 17.1 g (0.05 mole) of diphenyltin dichloride in 20 ml of THF. The addition was made over 1 h. The reaction mixture was allowed to stir overnight at room temperature and then at the reflux temperature for 3 h. The reaction mixture was worked up anhydrously by removing the organic solvent on a rotary evaporator. Sodium-dried benzene was added to the residue and the insoluble inorganic material was separated by filtration. The filtrate, upon concentration, gave a solid melting at 233–237°. After two recrystallizations from benzene, the m.p. was raised to 237–240°. The yield was 15.1 g. (39.7%) of bis(pentachlorophenyl)diphenyltin. The ultraviolet spectrum in cyclohexane gave λ_{max} 219 mμ (ε 116,900), 291 mμ (ε 1255) and 301 mμ (ε 1255). [Found: Sn, 14.88, 14.95; mol.wt. (vapor pressure osmometer), 841. $C_{24}H_{10}Cl_{10}Sn$ calcd.: Sn, 15.36%; mol.wt., 772.] The low Sn analyses and the high result for the molecular weight determination suggested that the compound contained a small percentage of hexachlorobenzene or that the compound formed a complex with benzene. The sample was dried in a "drying pistol" at 100° overnight before the analyses were made.

Reaction between pentachlorophenylmagnesium chloride and phenyltin trichloride

Pentachlorophenylmagnesium chloride (0.1 mole) in 100 ml of THF was added slowly to 9.06 g (0.03 mole) of phenyltin trichloride in 40 ml of sodium-dried xylene. Heat was evolved during the addition and solids were precipitated. The reaction mixture was stirred overnight at room temperature and then for 3 h at the reflux temperature. The THF was removed from the reaction mixture and replaced by xylene. The mixture was refluxed for an additional 3 h and then filtered to separate the insoluble material, m.p. 400–401° (0.8 g). The xylene filtrate, upon concentration, gave an oily residue. No further work was carried out with this black oil.

Preparation of tetrakis(pentachlorophenyl)tin

Pentachlorophenylmagnesium chloride (0.1 mole) in 100 ml of THF was added dropwise to 4.0 g (0.015 mole) of tin tetrachloride in 20 ml of sodium-dried hexane. Heat was evolved and much white solid was formed. The reaction mixture was stirred at room temperature for 3 h and at the reflux temperature for 2 h. At this stage, sodium-dried xylene was added and the THF was distilled off slowly. Again, the reaction mixture was refluxed for 2 h with xylene as the solvent. Finally, the solution was hydrolyzed with aqueous ammonium chloride solution and the insoluble material was separated by filtration. When heated in a capillary tube, it decomposed without melting at 300°. It was insoluble in the common organic solvents and only slightly soluble in the high boiling xylene (about 0.5 g per 100 ml xylene). It was then extracted several times with water and then ethanol to assure the complete removal of any inorganic salts. When a sample was ignited it burned, showing the presence of carbon. A sample was boiled in xylene and then filtered. The filtrate, upon concentration, gave some fine, light brown, powdery solids, m.p. 446–449° (decomposed to a black solid). [Found: Sn 10.76, 10.56; mol.wt. (mass spectrum), 1100±10. $C_{24}Cl_{20}Sn$ calcd.: Sn, 10.62%; mol.wt., 1106.]

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SUMMARY

The preparations of some pentachlorophenyl derivatives of silicon and tin by the interaction of pentachlorophenylmagnesium chloride with various chlorosilanes and chlorostannanes were described. It was found that a halogen–metal exchange reaction was operating as well as the coupling reaction. The ultraviolet properties of these derivatives were studied and it was found that each of these pentachlorophenyl derivatives possessed an absorption band at about 220 mμ with unusually high molar absorptivity. It was also observed that the molar absorptivities of these compounds increased as the number of pentachlorophenyl groups in the compounds increased. In general, the tin derivatives had higher molar absorptivities than those of the corresponding silicon derivatives.

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