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POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS
XXV*. THE METALATION OF SOME PENTACHLOROPHENYL-SUBSTITUTED ORGANOSILICON COMPOUNDS

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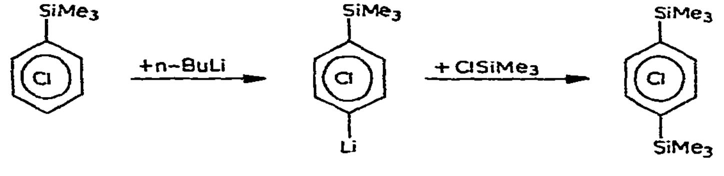
SUMMARY

Bis(pentachlorophenyl)dimethylsilane and 1,3-bis(pentachlorophenyl)tetramethyldisiloxane can be metalated with n-butyllithium in THF at low temperature to give organolithium reagents, in which the lithium atom is in the *para*-position to the silicon atom. Several compounds were obtained by treating the organolithium reagents thus formed, with chlorotrimethylsilane, 1,3-dichlorotetramethyldisiloxane, dimethyldichlorosilane and dimethylchlorosilane. Some of the organosilicon compounds reported were prepared by two alternative routes to prove further the proposed structures.

INTRODUCTION

The preparation of pentachlorophenyllithium[3,4] and pentachlorophenylmagnesium chloride[5-8] made possible the synthesis of several organosilicon derivatives, containing pentachlorophenyl groups[1,2,9-13]. During the investigation of these types of compounds it was found in this laboratory[14] that (trimethylsilyl)pentachlorobenzene (I) can be metalated with n-butyllithium in tetrahydrofuran (THF) at −70° to give *p*-lithio(trimethylsilyl)tetrachlorobenzene (II), which on derivatization with chlorotrimethylsilane gave *p*-bis(trimethylsilyl)tetrachlorobenzene (III)***:



(I) (II) (III)

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* For a preliminary communication see ref. 1; for Part XXIV see ref. 2.

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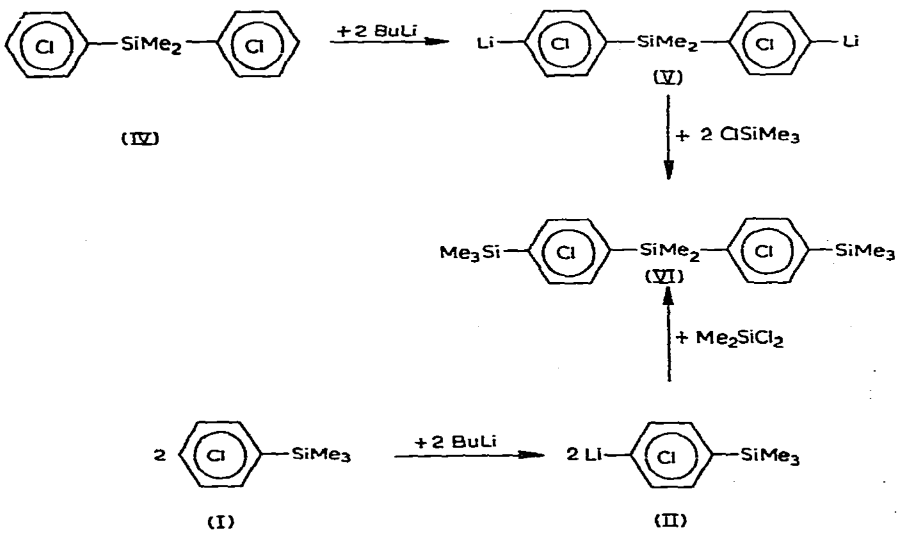
*** For purpose of brevity the following symbol will be used in this paper for the perchlorinated aromatic nucleus:  Only substituents other than chlorine will be indicated.

This reaction suggests that other organosilicon compounds, containing pentachlorophenyl groups may behave similarly. We now wish to report some examples of this metalation applied to several other compounds, containing C_6Cl_5 groups.

RESULTS AND DISCUSSION

In order to obtain difunctional derivatives which could be of interest in the synthesis of thermostable polymers, we have investigated the metalation of two compounds, containing two pentachlorophenyl groups in the molecule. Thus, dimethylbis(pentachlorophenyl)silane[10] and bis(pentachlorophenyl)tetramethyldisiloxane[1,2] were treated with n-butyllithium, in THF at −65 to −70°. It was found that in both cases the chlorine atoms in the *para*-position to the silicon atoms were exchanged for lithium. The organolithium compounds thus prepared were derivatized *in situ* with trimethylchlorosilane, to give the corresponding trimethylsilyl derivatives. Some reactions with other chlorosilanes were also investigated.

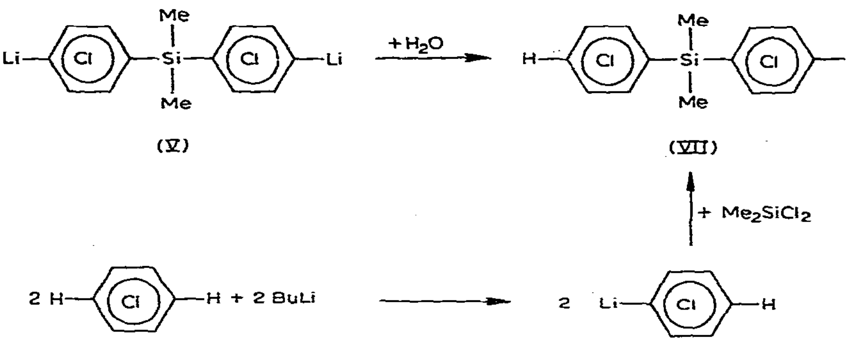
By the metalation of bis(pentachlorophenyl)dimethylsilane (IV) with butyllithium in THF, at −70°, the *p,p'*-dilithio compound (V) is obtained. On treatment with chlorotrimethylsilane, (V) gives bis[(*p*-trimethylsilyl)tetrachlorophenyl]dimethylsilane (VI). The same compound can be obtained by an alternative route, from the organolithium compound (II) and dimethyldichlorosilane:



The trimethylsilyl derivative (VI) can be separated only with difficulty as a crystalline compound. After removing the solvent the residue is an oil, from which (VI) crystallizes only after long standing. However, it can be recrystallized from acetone, to give crystals with m.p. 184–186°, but evaporation of a solution of (VI) in petroleum ether (b.p. 60–70°) always yields an oil, which crystallizes only with difficulty on standing.

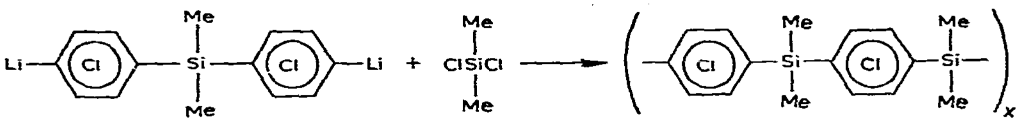
We feel that the formation of compound (VI) by two different routes serves as a convincing structure proof. To obtain further confirmation of the structure, and to establish without any doubt the position of the aromatic nucleus where the halogen–

metal exchange takes place, a sample of the organolithium compound (V) was subjected to hydrolysis. This gave bis(2,3,5,6-tetrachlorophenyl)dimethylsilane (VII), a compound which was also prepared by the reaction of 1-lithio-2,3,5,6-tetrachlorobenzene[3] with dimethyldichlorosilane:



Thus, the formation of compound (VII) in both cases, proves that the metalation (here halogen–metal exchange) occurs in *para*-position to the silicon atom, in all pentachlorophenyl derivatives of silicon, investigated so far, under the conditions mentioned above.

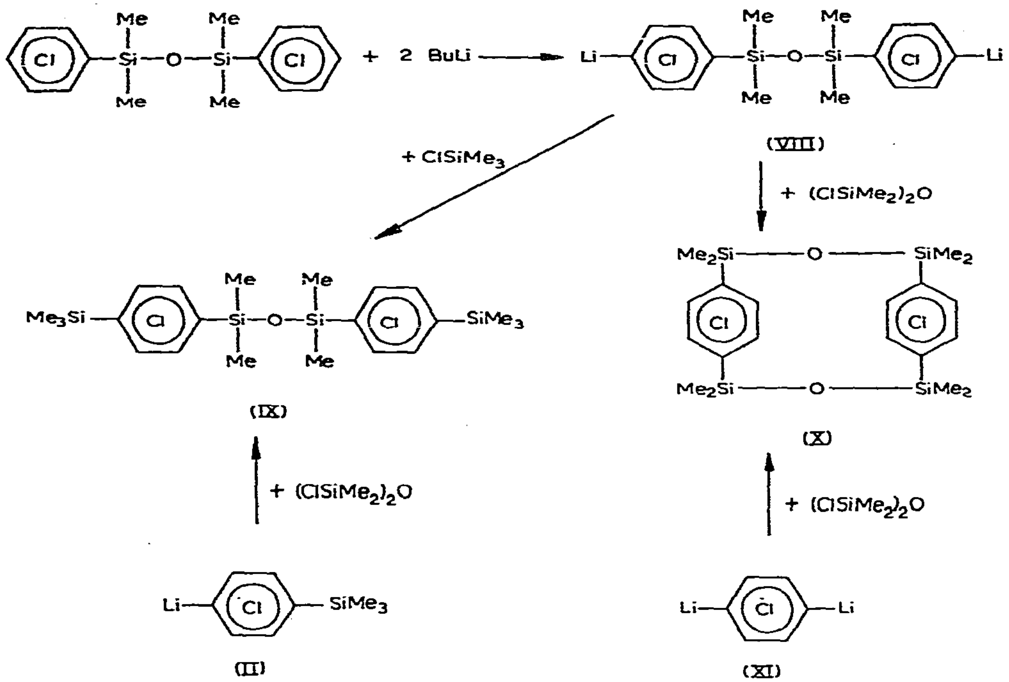
To explore the possibility of using *p,p'*-dilithioperchloro-aromatic organosilicon derivatives in the synthesis of new types of polymers, the dilithio derivative (V) was reacted with dimethyldichlorosilane. This reaction gave a foam-like polymeric material, softening between 125 and 150°, which probably has the structure shown below:



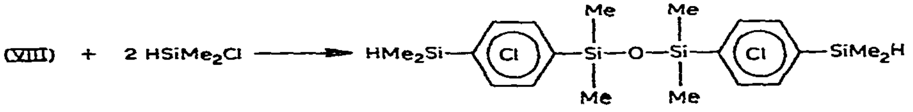
This polymer has not been investigated further in this laboratory.

In quite a similar manner, the metalation of 1,3-bis(pentachlorophenyl)tetramethyldisiloxane with n-butyllithium in THF at −70°, gave a *p,p'*-dilithio-substituted derivative (VIII). By treating this compound *in situ* with chlorotrimethylsilane, the corresponding *p,p'*-trimethylsilyl derivative (IX) was obtained. As an application of this metalation, a cyclic compound (X) was also prepared, by treating the organolithium compound (VIII), with 1,3-dichlorotetramethyldisiloxane. The cyclic compound is accompanied in the reaction product by an insoluble, infusible, probably polymeric material (see also the previous paper[2]). Both compounds (IX) and (X), were also prepared by alternative routes, as shown in the scheme below, from 1,3-dichlorotetramethyldisiloxane and *p*-$LiC_6Cl_4SiMe_3$ (II) and *p*-LiC_6Cl_4Li (XI), respectively.

By using the same metalation reaction, 1,3-bis(pentachlorophenyl)tetramethyldisiloxane can be converted into other types of compounds, which may be of interest for the synthesis of polymeric materials, *e.g.*, compounds containing -SiR_2H groups. As an example the organolithium compound (VIII), was treated with di-



methylchlorosilane to give 1,3-bis[(*p*-dimethylsilyl)tetrachlorophenyl]tetramethyldisiloxane, (XII):



(XII)

The compounds reported here were identified by elemental analysis and molecular weight determinations (mass spectrometry). The ultraviolet absorption spectra of the several compounds described here were discussed elsewhere[15].

EXPERIMENTAL

All reactions involving organolithium derivatives were performed under an atmosphere of oxygen-free dry nitrogen. The solvents were dried over metallic sodium and distilled before use from sodium benzophenone ketyl. The glassware was dried in an oven at 130°, assembled while hot and purged with a stream of dry nitrogen. All the reagents were commercial products, except 1,3-dichlorotetramethyldisiloxane, which has been prepared from dimethyldichlorosilane and absolute ethanol in the presence of ferric chloride as catalyst[16]. Melting points are uncorrected.

1,3-*Bis*[(*p-trimethylsilyl*)*tetrachlorophenyl*]*dimethylsilane* (*VI*)

(*a*) *By the metalation of bis*(*pentachlorophenyl*)*dimethylsilane*. A suspension of 5.6 g (0.01 mole) of bis(pentachlorophenyl)dimethylsilane (IV) in 200 ml dry THF was cooled to −70° by a Dry-Ice/acetone mixture and was treated with 12.5 ml of a solution containing 1.28 g (0.02 mole) n-butyllithium in n-hexane, added dropwise during 10 min under stirring. The reaction mixture was stirred for an additional hour at −70°, until Color Test II[17] was negative and Color Test I[18] was positive, indicating the disappearance of n-butyllithium and the formation of a new organolithium derivative, (V). The solution was then treated with 2.16 g (0.02 mole) of chlorotrimethylsilane, stirred for an additional hour, until Color Test I was negative, and allowed to reach room temperature. The mixture was evaporated in a rotary evaporator, to give a mixture of oil and salt (LiCl). The mixture was extracted with benzene and the solution evaporated again to give 4.7 g of a viscous oil. After long standing the oil solidified almost completely, but attempts to recrystallize the solid from petroleum ether (b.p. 60–70°) gave again the same oil, which failed to crystallize. The solid formed after long standing of this oil was recrystallized from acetone, to give 1.1 g (17.4% yield) of 1,3-bis[(*p*-trimethylsilyl)tetrachlorophenyl]dimethylsilane (VI), m.p. 184–186° (Found: C, 37.5; H, 3.4; Si, 13.0; mol.wt. by mass spectrometry, 632. $C_{20}H_{24}Cl_8Si_3$ calcd.: C, 37.9; H, 3.8; Si, 13.3%; mol.wt., 632.)

(*b*) *By the metalation of (pentachlorophenyl)trimethylsilane.* A solution of 3.22 g (0.01 mole) of (pentachlorophenyl)trimethylsilane (I) in 100 ml diethyl ether was cooled to −70° with Dry-Ice/acetone mixture and then was treated with 6.5 ml of a solution containing 0.64 g (0.01 mole) of n-butyllithium in 6.5 ml n-hexane, added dropwise and stirred for 1 h, until Color Test II[17] was negative. Then the solution was treated with 2.0 ml dimethyldichlorosilane, stirred for 1 h until Color Test I[18] was negative, and allowed to reach gradually the room temperature and evaporated. The mixture of oil and solid thus obtained was extracted with petroleum ether (b.p. 60–70°), the solution was evaporated, and the residue was recrystallized from acetone, to give 1.3 g (41.1%) of 1,3-bis[(*p*-trimethylsilyl)tetrachlorophenyl]dimethylsilane (VI), m.p. 184–186°, mixed m.p. 184–186°. An additional amount of 0.3 g was recovered by further concentration of the solution, the yield thus becoming 1.6 g (50.6%).

Bis(2,3,5,6-*tetrachlorophenyl*)*dimethylsilane* (*VII*)

(*a*) *By the metalation of* 1,2,4,5-*tetrachlorobenzene.* A solution of 21.6 g (0.1 mole) of 1,2,4,5-tetrachlorobenzene in 150 ml dry THF was cooled at −70° and treated with 64 ml of a 15% solution of n-butyllithium in n-hexane (containing 0.1 mole of n-BuLi), stirred for 90 min, and treated with 6.5 g (0.05 mole) of dimethyldichlorosilane, and then stirred for an additional hour. The mixture was allowed to reach room temperature, concentrated to dryness, and the solid was sublimed at 180–200°/0.2 mm, to give 11 g of crystals (VII), m.p. 248–252°. After recrystallization from petroleum ether (b.p. 60–70°), pure bis(2,3,5,6-tetrachlorophenyl)dimethylsilane, (VII), m.p. 268–269°, was obtained. (Found: C, 34.0; H, 1.2; mol.wt. by mass spectrometry, 488. $C_{14}H_8Cl_8Si$ calcd.: C, 34.4; H, 1.6%; mol.wt., 488.)

(*b*) *By the hydrolysis of organolithium compound* (*V*). The organolithium reagent (V) was prepared as above, from 5.6 g, (0.01 mole) of bis(pentachlorophenyl)dimethylsilane and 0.02 mole n-butyllithium. The solution was hydrolysed with dilute hydrochloric acid, extracted with diethyl ether and evaporated. The residue was recrystallized from petroleum ether (b.p. 60–70°) to give 3.2 g (65.5%) of bis(2,3,5,6-tetrachlorophenyl)dimethylsilane (VII), m.p. 268–269°.

Polymeric $(-C_6Cl_4-SiMe_2-C_6Cl_4-SiMe_2-)_x$

A solution of 5.6 g (0.01 mole) of bis(pentachlorophenyl)dimethylsilane (IV), in 125 ml THF, cooled at −65°, was treated with 12.5 ml solution of n-BuLi in n-hexane (15%) and after 1 h of stirring at low temperature, was treated with 1.3 ml (0.01 mole) of dimethyldichlorosilane. After 5 h of stirring the Color Test I[18] was negative and the solution was evaporated. The residue was extracted with benzene, and after removing the solvent 4.0 g (73% yield) of a polymeric, foam-like material, softening at 125–150°, was obtained.

1,3-*Bis*[(*p-trimethylsilyl*)*tetrachlorophenyl*]*tetramethyldisiloxane* (*IX*)

(*a*) *By the metalation of* 1,3-*bis*(*pentachlorophenyl*)*tetramethyldisiloxane*. A solution of 6.3 g (0.01 mole) of 1,3-bis(pentachlorophenyl)tetramethyldisiloxane in 150 ml THF, cooled at −70°, was treated with 13 ml of a solution of n-BuLi (15%) in n-hexane, stirred for 1 h and treated with 2 ml of chlorotrimethylsilane, diluted with 50 ml petroleum ether (b.p. 60–70°) and stirred for 1 h. The mixture was then allowed to reach room temperature, evaporated to dryness, and the residue was extracted with petroleum ether (b.p. 60–70°). The solution was chromatographed over neutral alumina, to give after evaporation of the solvent 0.9 g (12.7%) of crude 1,3-bis[(*p*-trimethylsilyl)tetrachlorophenyl]tetramethyldisiloxane (IX), m.p. 78–80°. Recrystallization from acetone gave (IX), m.p. 86–87°. (Found: C, 37.5; H, 3.9; mol.wt. by mass spectrometry, 706. $C_{22}H_{30}Cl_8OSi_4$ calcd.: C, 37.4; H, 4.2%; mol.wt., 706.5.)

(*b*) *By the metalation of* (*pentachlorophenyl*)*trimethylsilane*. An organolithium reagent (II) prepared as described above, from 16.1 g (0.05 mole) of (pentachlorophenyl)trimethylsilane (I) in 150 ml THF and 34 ml solution of n-BuLi (15%) in n-hexane, at −70°, was treated with 5.0 g (0.025 mole) of 1,3-dichlorotetramethyldisiloxane, diluted with 50 ml petroleum ether (b.p. 60–70°). Work-up as above resulted in the isolation of 3.6 g (20.4%) of crystals of (IX), m.p. 60–68°, which after recrystallization from acetone gave pure 1,3-bis[(*p*-trimethylsilyl)tetrachlorophenyl]-tetramethyldisiloxane, (IX), m.p. 87°, mixed m.p. 86–87°.

Cyclobis[*p*-(*tetrachlorophenylene*)*tetramethyldisiloxane*] (*X*)

An organolithium reagent (VIII) was prepared as described above, from 6. 3 g (0.01 mole) of 1,3-bis(pentachlorophenyl)tetramethyldisiloxane, suspended in 100 ml THF, and 12.8 ml of a 15% solution of n-BuLi in n-hexane. This was treated with 2.0 g (0.01 mole) of 1,3-dichlorotetramethyldisiloxane, diluted with 50 ml diethyl ether, and stirred until Color Test I[18] was negative. The solution was evaporated to dryness and the residue was extracted with petroleum ether (b.p. 60–70°) in a Soxhlet apparatus and the solution evaporated, to give 1.1 g (15.8%) of cyclobis[*p*-(tetrachlorophenylene)tetramethyldisiloxane] (X), m.p. 401–402°. Mixed m.p. with a sample prepared as described in the previous paper[2] [from compound (XI)] was 401–402°.

1,3-*Bis*[(*p-dimethylsilyl*)*tetrachlorophenyl*]*tetramethyldisiloxane* (*XII*)

An organolithium reagent (VIII) prepared as described above, from 12.6 g (0.02 mole) 1,3-bis(pentachlorophenyl)tetramethyldisiloxane in 200 ml THF, and 25.6 ml of a solution of n-BuLi in n-hexane (15%), was treated with 8 ml (excess) of chlorodimethylsilane, diluted with 10 ml THF. The mixture was stirred for 1 h at

−70°, and then allowed to reach room temperature. The solvent was evaporated on a rotary evaporator, the residue was extracted with petroleum ether (b.p. 60–70°) and concentrated to give a mixture of oil and solid. This was recrystallized from ethanol–benzene mixture, to give 8.7 g of 1,3-bis[(*p*-dimethylsilyl)tetrachlorophenyl]-tetramethyldisiloxane (XII), m.p. 88–90°. (Found: C, 35.6; H, 3.9; Si, 15.9; mol.wt. by mass spectrometry, 678. $C_{10}H_{26}Cl_8OSi_4$ calcd.: C, 35.4; H, 3.8; Si, 16.2%; mol. wt., 678.)

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