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POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS
XXIV*. PERHALOARROMATIC ORGANOSILOXANES

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SUMMARY

From the reaction of pentahalogenophenyllithium and pentachlorophenylmagnesium chloride with α,ω-dichloropolysiloxanes, linear di- and tri-siloxanes, end-blocked with perhaloaromatic groups were prepared. Siloxane analogs of paracyclophanes were prepared by the reaction of 1,3-dichlorotetramethyldisiloxane with 1,4-dilithio-2,3,5,6-tetrahalobenzene. Infrared spectral data are given for some of the compounds reported.

INTRODUCTION

The recent interest in organometallic and organometalloidal compounds, containing pentafluorophenyl[3] and pentachlorophenyl[4] groups has been greatly facilitated by the availability of pentachlorophenylmagnesium chloride[5-8], pentachlorophenyllithium[9,10], and pentafluorophenyllithium[11]. Thus, several organosilicon compounds containing pentachlorophenyl groups were reported in a short period of time: tetrakis(pentachlorophenyl)silane[4], (pentachlorophenyl)phenylsilanes $(C_6Cl_5)_nPh_{4-n}Si$ ($n=1$ and 2)[4], α,ω-bis(pentachlorophenyl)poly(dimethylsilanes) $C_6Cl_5(SiMe_2)_nC_6Cl_5$ ($n=1$–6)[12], (pentachlorophenyl)halosilanes $(C_6Cl_5)_nSiX_{4-n}$ ($X=F$, $n=3$; $X=Cl$, $n=2$)[13], phenyl(pentachlorophenyl)halosilanes $(C_6Cl_5)_nPh_{3-n}SiCl$ ($n=1$ and 2)[14], and other derivatives (*e.g.*, $C_6Cl_5SiMe_2Cl$)[1,15]. Similarly, a number of organosilicon compounds, containing pentafluorophenyl groups have been prepared, including tetrakis(pentafluorophenyl)silane[16,17], (pentafluorophenyl)trimethylsilane[18-20], phenyl(pentafluorophenyl)silanes $(C_6F_5)_nPh_{4-n}Si$ ($n=1$–4)[21], phenyl(pentafluorophenyl)halosilanes $(C_6F_5)_nPh_{3-n}SiX$ ($n=1$–2, $X=Cl$; also $X=H$)[21], methyl(pentafluorophenyl)silanes $(C_6F_5)_nMe_{3-n}SiH$ ($n=1$ or 2)[22], methyl(pentafluorophenyl)ethoxysilanes $(C_6F_5)_nMe_{2-n}Si(OEt)_2$ ($n=1$ or 2)[22], dimethyl(pentafluorophenyl)chlorosilane[1,15].

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

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RESULTS AND DISCUSSION

We wish now to report the preparation of several perhaloaromatic organosiloxanes. Compounds containing pentachlorophenyl groups were prepared by the reaction of either pentachlorophenyllithium or pentachlorophenylmagnesium chloride with 1,3-dichlorotetramethyldisiloxane and 1,5-dichlorohexamethyltrisiloxane. In both cases the starting haloaromatic compound was hexachlorobenzene, which can be readily converted into the appropriate organolithium[9] or Grignard[5] reagent. Compounds containing pentafluorophenyl groups were obtained via metalation of pentafluorobenzene[11], which gives C_6F_5Li, and this reagent was then reacted with the appropriate α,ω-dichlorosiloxane. Thus, bis(pentachlorophenyl)- and bis(pentafluorophenyl)organosiloxanes were obtained:

$$2\,C_6X_5M + Cl(Me_2SiO)_nSiMe_2Cl \rightarrow C_6X_5(Me_2SiO)_nSiMe_2C_6X_5 + 2\,MCl$$

$$\begin{array}{ll} X = Cl;\ M = Li;\ n = 1 \text{ and } 2 & (Ia),\ n = 1 \\ X = Cl;\ M = MgCl;\ n = 1 \text{ and } 2 & (Ib),\ n = 2 \\ X = F;\ M = Li;\ n = 1 \text{ and } 2 & \end{array}$$

In the case of pentachlorophenyl derivatives, prepared with both Grignard and organolithium reagents, the use of organolithium compounds has little effect upon the yield, but it has the advantage that no dark by-products are formed, as in the case of Grignard reagents, and therefore, the purification of the products is much easier.

The disiloxanes were also prepared by alternative routes[1,15]. Thus, 1,3-bis(pentachlorophenyl)tetramethyldisiloxane was obtained by the condensation of (pentachlorophenyl)dimethylsilanol with (pentachlorophenyl)dimethyl(dimethylamino)silane, while 1,3-bis(pentachlorophenyl)tetramethyldisiloxane was prepared by the hydrolysis of (pentafluorophenyl)dimethylchlorosilane[1,15].

$$C_6Cl_5SiMe_2OH + C_6Cl_5SiMe_2NMe_2 \rightarrow C_6Cl_5SiMe_2OSiMe_2C_6Cl_5 + HNMe_2$$

$$2\,C_6F_5SiMe_2Cl + H_2O \rightarrow C_6F_5SiMe_2OSiMe_2C_6F_5 + 2\,HCl$$

The disiloxanes prepared by different routes were found identical.

It was shown that 1,2,4,5-tetrachlorobenzene can be metalated by n-butyllithium in tetrahydrofuran (THF) at −70° to give 3,6-dilithio-1,2,4,5-tetrachlorobenzene[10]. A similar reaction was reported for 1,2,4,5-tetrafluorobenzene[11]. We used the dilithio derivatives thus obtained to prepare cyclic compounds, containing perhalogenated *p*-phenylene groups, bridged with tetramethyldisiloxane units (II). The term cyclobis(*p*-phenylenetetramethyldisiloxanes) is used here to designate these compounds*. Such compounds are siloxane analogs of paracyclophanes[23,24] and a non-halogenated analog (X=H) has been previously reported[25,26].

Both compounds (II) (X=F and Cl) are crystalline solids. The chloro derivative has an unusual high melting point (401–402°).

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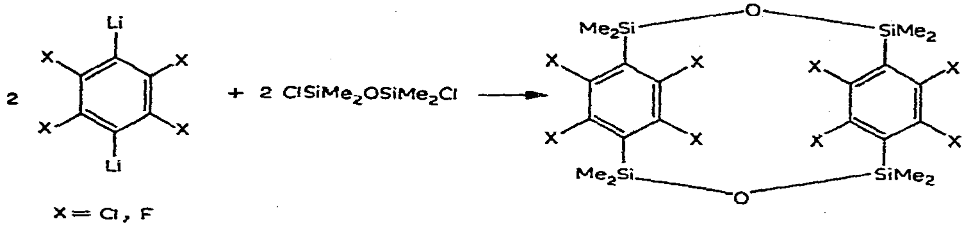
* The rational name suggested by Chemical Abstracts Service for (II), X = F would be: 6,7,13,14,15,16,17,18-octafluoro-2,2,4,4,9,9,11,11-octamethyl-3,10-dioxa-2,4,9,11-tetrasilatricyclo[10.2.2.2^{5,8}]octadeca-5,6,12,14,15,17-hexaene (Nomenclature Director, Chemical Abstracts; private communication). Although such a name may be accepted for indexing purposes, a shorter name seemed desirable for current use.



(II)

The ultraviolet spectrum of the non-halogenated (II) ($X = H$)[25] suggested that the two aromatic rings suffer a deformation, due to the strain in the transannular system. A comparison of the UV spectra of the halogenated derivatives (II) ($X = Cl$ and F) with those of other related compounds (linear) was made in ref. 27. Thus, it was found that in the UV spectra of the cyclic compounds (II) ($X = Cl$ and F) the *B* bands of the aromatic nucleus exhibit bathochromic shifts, as compared to the spectra of the related noncyclic compounds. This can be interpreted in terms of a deformation of the aromatic nucleus and/or in terms of some transannular electronic interaction of the two aromatic rings[27].

The infrared spectra of the four disiloxanes described here [(Ia) and (II), $X =$ Cl and F] were recorded for comparison. The absorption bands found are those expected for compounds having the composition and structure assumed (see Experimental Part). It would be highly interesting to compare the frequencies of the Si–O–Si unsymmetrical bond stretching in these compounds. In the linear compounds (Ia), two sharp bands occur in the 1100–1000 cm^{-1} region, where the absorption mentioned should be looked for: at 1080 and 1100 cm^{-1} [in (Ia), $X = F$] and 1085 and 1093 cm^{-1} [in (Ia), $X = Cl$]. The cyclic compounds exhibit in this region only one band each at 1064 cm^{-1} [(II), $X = F$] and 1080 cm^{-1} [(II), $X = Cl$]. However, care should be exercised in interpreting these bands, because tetrakis(pentafluorophenyl)-silane also shows a sharp band at 1098 cm^{-1} (ref. 17), which probably is associated with the perhaloaromatic nucleus. Possibly the bands at 1080 cm^{-1} [in (Ia), $X = F$] and 1085 cm^{-1} [in (Ia), $X = Cl$] are due to unsymmetrical Si–O–Si bond stretching vibrations, but a certain assignment seems rather difficult to be made under the circumstances mentioned.

The molecular weights of the compounds reported here were determined by mass spectrometry. The compounds exhibit peaks due to the parent molecular ions, as well as peaks due to the loss of methyl groups and Si–O bond cleavage.

EXPERIMENTAL

All the syntheses involving the use of organolithium or Grignard reagents were performed in an oxygen-free nitrogen atmosphere, under anhydrous conditions. The glassware was dried in an oven at 130°, assembled while hot and purged with a stream of dry nitrogen before introducing the reagents. The reagents used were commercial products, except 1,3-dichlorotetramethyldisiloxane and 1,5-dichlorohexamethyltrisiloxane, which were prepared from dimethyldichlorosilane and ethanol, in the presence of ferric chloride[30]. Melting points are uncorrected.

1,3-Bis(pentachlorophenyl)tetramethyldisiloxane [*(Ia), X = Cl*]

(*a*) *By using the organolithium reagent.* A solution of pentachlorophenyllithium was prepared by treating a suspension of 28.5 g (0.1 mole) hexachlorobenzene in 150 ml THF, cooled to −70° with Dry-Ice/acetone mixture, with 64 ml solution containing 0.1 mole n-butyllithium in n-hexane, and stirring for 20 min, until Color Test II[31] was negative, showing the consumption of n-butyllithium. To this solution 10.1 g (0.05 mole) of 1,3-dichlorotetramethyldisiloxane, diluted with 50 ml THF were added dropwise, during 15 min at low temperature, stirred for 2 h until Color Test I[32] was negative, and allowed to reach room temperature. The solution was evaporated to dryness, the residue was extracted with petroleum ether (b.p. 60–70°) and the solution was evaporated to give 20.9 g (66.3 %) of 1,3-bis(pentachlorophenyl)tetramethyldisiloxane, m.p. 165° (from ethanol or petroleum ether, b.p. 60–70°). (Found: C, 30.9; H, 2.1; Si, 8.8; mol. wt. by mass spectrometry, 631. $C_{16}H_{12}Cl_{10}OSi_2$ calcd.: C, 30.4; H, 1.9; Si, 8.9 %; mol. wt., 631.)

(*b*) *By using the Grignard reagent.* A Grignard reagent was prepared from 57.0 g (0.2 mole) of hexachlorobenzene and 4.2 g magnesium (0.2 g-atom) in 200 ml THF, and then 20.3 g (0.1 mole) of 1,3-dichlorotetramethyldisiloxane was added dropwise and the mixture stirred for 1.5 h. The dark solution was hydrolysed with dilute hydrochloric acid and the precipitate formed was filtered, to give 24.3 g (52.6 %) of 1,3-bis(pentachlorophenyl)tetramethyldisiloxane, m.p. 162–163°. The filtrate was dried over sodium sulphate and chromatographed over neutral alumina and evaporated, to give another crop of 10.3 g crystals, m.p. 165° (from ethanol), mixed m.p. 165°. The total yield of 1,3-bis(pentachlorophenyl)tetramethyldisiloxane was 40.2 g (63.7 %).

1,3-Bis(pentafluorophenyl)tetramethyldisiloxane [*(Ia), X = F*]

Pentafluorophenyllithium was prepared from 16.8 g (0.1 mole) of pentafluorobenzene and 64 ml solution of n-butyllithium in n-hexane (15 %), containing 0.1 mole n-BuLi, in 150 ml anhydrous THF at −65°. A solution of 10.16 g (0.05 mole) of 1,3-dichlorotetramethyldisiloxane in 50 ml petroleum ether (b.p. 60–70°) was added dropwise to the organolithium reagent, under stirring and cooling by a Dry-Ice/acetone mixture. The reaction mixture was allowed to reach room temperature, the solution was concentrated and the residue was extracted with petroleum ether (b.p. 60–70°), the solvent was evaporated and the colorless liquid crystallized after a few hours of standing to give 17.5 g (75.1 %) of 1,3-bis(pentafluorophenyl)tetramethyldisiloxane, m.p. 41°. (Found: C, 41.4; H, 2.9; Si, 11.7; mol. wt. by mass spectrometry, 466. $C_{16}H_{12}F_{10}OSi_2$ calcd.: C, 41.2; H, 2.6; Si, 12.0 %; mol. wt., 466.)

1,5-Bis(pentachlorophenyl)hexamethyltrisiloxane [*(Ib), X = Cl*]

(*a*) *By using the Grignard reagent.* A Grignard reagent prepared as above from 57.0 g (0.2 mole) hexachlorobenzene in 150 ml THF, was treated with 27.7 g (0.1 mole) of 1,5-dichlorohexamethyltrisiloxane. The reaction mixture was worked up as above to give 38.7 g (48.7 %) of 1,5-bis(pentachlorophenyl)hexamethyltrisiloxane, m.p. 72–73° (from petroleum ether, b.p. 60–70°). (Found: C, 30.9; H, 2.9; Si, 11.4. $C_{22}H_{18}Cl_{10}O_2Si_3$ calcd.: C, 30.6; H, 2.6; Si, 11.8 %.)

(*b*) *By using the organolithium reagent.* Pentachlorophenyllithium was prepared as above from 11.4 g (0.04 mole) hexachlorobenzene in 100 ml THF, and

26 ml solution of n-butyllithium in n-hexane (15%) at −65°. The solution was treated with 5.6 g (0.02 mole) of 1,5-dichlorohexamethyltrisiloxane diluted with 50 ml THF stirred for 30 min, at −65° until Color Test I was negative and allowed to reach room temperature. After evaporating the solvent and extracting the residue with petroleum ether (b.p. 60–70°) 8.8 g (54.7%) of 1,5-bis(pentachlorophenyl)hexamethyltrisiloxane, m.p. 70° was obtained. A recrystallization from petroleum ether (b.p. 60–70°) gave m.p. and mixed m.p. 72–73°.

1,5-Bis(pentafluorophenyl)hexamethyltrisiloxane [(*Ib*), *X*=*F*]

A solution of pentafluorophenyllithium prepared as above was treated with 13.9 g (0.05 mole) of 1,5-dichlorohexamethyltrisiloxane diluted with 50 ml THF, at −65° stirred for 20 min, until Color Test I was negative and allowed to reach room temperature. The solution was concentrated in a rotary evaporator, the residue was extracted with petroleum ether (b.p. 60–70°) to give after removing the solvent 19.8 g (73.3%) of crude 1,5-bis(pentafluorophenyl)hexamethyltrisiloxane. The VPC showed this product to be essentially pure, with two minor peaks corresponding to unidentified impurities. By distilling the product on a Nester–Faust spinning band column, 16.1 g of pure 1,5-bis(pentafluorophenyl)hexamethyltrisiloxane, b.p. 60–62°/15 mm (purity confirmed by VPC) was obtained. (Found: C, 40.1; H, 3.9; Si, 15.3. $C_{18}H_{18}F_{10}O_2Si_3$ calcd.: C, 39.9; H, 3.6; Si, 15.5%.)

Cyclobis[p-(tetrachlorophenylene)tetramethyldisiloxane] [(*II*), *X*=*Cl*]

An organolithium reagent was prepared from 21.6 g (0.1 mole) of 1,2,4,5-tetrachlorobenzene in 150 ml THF and 128 ml solution of n-butyllithium in n-hexane (15%) containing 0.2 mole active substance at −65°. After Color Test II was negative, 20.3 g (0.1 mole) of 1,3-dichlorotetramethyldisiloxane diluted with 75 ml THF was added dropwise, during 1 h; the mixture was stirred for an additional 30 min, until Color Test I was negative, and the precipitate was filtered. A yield of 12.6 g (36.7%) of solid material was obtained, from which a portion was sublimed *in vacuo* at 350–370° to give cyclobis[*p*-(tetrachlorophenylene)tetramethyldisiloxane], m.p. 402°. Mixed m.p. with a sample prepared by an alternative route (see following paper[33]) was 402°. (Found: C, 35.1; H, 3.7; Si, 15.6; mol.wt. by mass spectrometry, 692. $C_{20}H_{24}Cl_8O_2Si_4$ calcd.: C, 34.7; H, 3.5; Si, 16.2%; mol.wt., 692.4.)

Cyclobis[p-(tetrafluorophenylene)tetramethyldisiloxane] [(*II*), *X*=*F*]

An organolithium reagent was prepared as above from 15.0 g (0.1 mole) of 1,2,4,5-tetrafluorobenzene and 128 ml solution of n-butyllithium in n-hexane (15%), in 150 ml THF at −65°. A solution of 20.3 g (0.1 mole) of 1,3-dichlorotetramethyldisiloxane in 100 ml petroleum ether (b.p. 60–70°) was added dropwise, under continuous stirring and cooling at −65°, during 1 h. The mixture was stirred for an additional 40 min, and then allowed to reach room temperature, concentrated and extracted with petroleum ether (b.p. 60–70°). After evaporating the solvent a mixture of solid and liquid products was obtained. The solid was filtered and recrystallized from benzene to give 1.6 g (5.7%) cyclobis[*p*-(tetrafluorophenylene)tetramethyldisiloxane] m.p. 238–239°. (Found: C, 42.6; H, 4.5; Si, 19.8; mol.wt. by mass spectrometry, 560. $C_{20}H_{24}F_8O_2Si_4$ calcd.: C, 42.8; H, 4.3; Si, 20.0%; mol.wt., 560.7.)

Infrared spectral data (w, weak; m, medium; b, broad; i, intense, but not sharp; s, sharp and intense; (sh), shoulder).

(*Ia*), $X = Cl$: 2950 w, 1510 s, 1460 i, 1415 m, 1370 m, 1277 s, 1266 s, 1259 s, 1126 (sh), 1100 i, 1080 i, 1050 (sh), 1015 w, 998 w, 970 s, 850 i, 823 (sh), 751 w, 743 w, 670 m.

(*Ia*), $X = F$: 2950 w, 1623 m, 1514 m, 1400 w, 1336 m, 1322 m, 1312 w, 1290 s, 1258 s, 1158 w, 1093 i, 1085 i, 870 i, 856 (sh), 830 m, 796 i, 740 w, 716 w, 702 w, 699 w, 677 w.

(*II*), $X = Cl$: 2950 w, 1610 w, 1438 i, 1418 s, 1400 s, 1340 w, 1262 s, 1259 i, 1225 s, 1064 i, 940 s, 930 m, 833 i, 797 i, 765 s, 731 s, 707 (sh), 697 m, 673 m.

(*II*), $X = F$: 2950 w, 1620 b, 1410 w, 1325 w, 1270 s, 1255 s, 1250 (sh), 1080 i, 835 i, 793 i, 745 b, 720 m, 697 m, 686 m.

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