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NOTE

POLYHALOORGANOMETALLIC- AND -ORGANOMETALLOIDAL COMPOUNDS
XXI*. (PENTACHLOROPHENYL)- AND (PENTAFLUOROPHENYL)DIMETHYLCHLOROSILANE

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In recent years organometallic and organometalloidal compounds, containing pentafluorophenyl[1] and pentachlorophenyl[2] groups have become a subject of extensive investigation. The synthesis of reactive intermediates, such as organochlorosilanes, containing polyhaloaromatic groups has been attempted in several cases[3,4,5]. Sometimes it was successful[4,5], but in other instances it was not possible to obtain such compounds[3]. Thus, attempts to prepare bis(pentafluorophenyl)dichlorosilane from silicon tetrachloride and the stoichiometric amount of pentafluorophenylmagnesium bromide, resulted in the formation of tetrakis(pentafluorophenyl)silane, irrespective of the mode of addition of the reagents[3]. To explain this behavior, it was suggested that substitution of a pentafluorophenyl group for chlorine on silicon activates the remaining chlorine atoms[3].

The reactions between dimethyldichlorosilane and pentafluoro- and pentachlorophenyllithium[6] resulted so far only in the formation of bis(pentahalophenyl)dimethylsilane, irrespective of the mode of addition of the reagents.

We now wish to communicate the successful synthesis of (pentachlorophenyl)- and (pentafluorophenyl)dimethylchlorosilane, two compounds which can be useful intermediates for further syntheses.

(Pentachlorophenyl)dimethylchlorosilane (I) was prepared by dropping a solution of pentachlorophenyllithium in THF[7], to a liberal excess of dimethyldichlorosilane (about tenfold), at −65°. The compound (I) can be readily obtained, after distilling the excess of dimethyldichlorosilane and THF, as a crystalline solid, m.p. 128°, in a 47% yield. In a similar way, (pentafluorophenyl)dimethylchlorosilane (II), was obtained in 28% yield, as a mobile liquid, b.p. 47°/1 mm. However, 70% of the starting C_6F_5Li was converted into bis(pentafluorophenyl)dimethylsilane, despite the very large excess of dimethyldichlorosilane. Thus, it appears that the activa-

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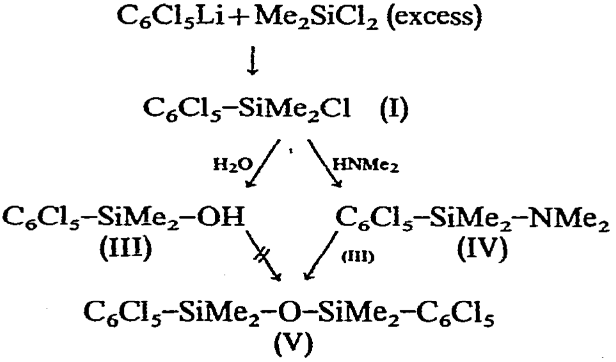
tion of the remaining chlorine atoms by introducing pentafluorophenyl groups finds further support in this observation. Also, it seems that the activation by a pentafluorophenyl group is more pronounced than the activation by a pentachlorophenyl group.

The chlorosilanes (I) and (II) were identified by elemental analysis (determination of hydrolysable chlorine), molecular weight determination (mass spectrometric) and conversion into other derivatives.

(Pentachlorophenyl)dimethylchlorosilane (I) is rather stable to hydrolysis (only minor hydrolysis was noticed after standing for 3 h at open atmosphere); however, in ethereal solution it can be hydrolysed to the corresponding silanol (III), m.p. 95–96° (in 71.4% yield). The silanol could not be converted into the corresponding disiloxane by heating. A dimethylamino derivative (IV), m.p. 166–167°, prepared from (I) and anhydrous dimethylamine, was condensed with the silanol (III) in benzene at reflux[8], to give 1,3-bis(pentachlorophenyl)tetramethyldisiloxane (V), m.p. 162–163°, also prepared by an alternative route[9] (from 1,3-dichlorotetramethyldisiloxane and pentachlorophenyllithium).



(Pentafluorophenyl)dimethylchlorosilane (II) is more sensitive to hydrolysis than (I). It reacts with water in diethyl ether, to give 1,3-bis(pentafluorophenyl)tetramethyldisiloxane (VI), m.p. 41°, prepared also by an alternative route[9]. In this case the isolation of the silanol failed.

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