# 1244. *Polyfluoroarenes. Part VII.*[1] *The Photochemical Reactions of Trichlorosilane and Trimethylsilane with Hexafluorobenzene*

By J. M. Birchall, W. M. Daniewski, R. N. Haszeldine, and L. S. Holden

Ultraviolet irradiation of trichlorosilane with hexafluorobenzene gives a good yield of dichlorofluoro(pentafluorophenyl)silane, $C_6F_5{\cdot}SiFCl_2$, hydrolysis of which yields pentafluorobenzene. The high-boiling fraction from this reaction consists mainly of compounds of the type $C_6F_4(SiFCl_2)_2$, and yields a mixture of tetrafluorobenzenes on hydrolysis. The photochemical reaction of trimethylsilane with hexafluorobenzene yields mainly trimethylpentafluorophenylsilane, fluorotrimethylsilane, and hydrogen; other products are probably cyclohexadiene derivatives, and displacement of a second fluorine atom to give the compounds $C_6F_4(SiMe_3)_2$ does not take place under the conditions employed.

The nucleophilic displacement of fluorine from polyfluoroarenes is now well established, and reactions of this type give rise to a wide range of polyfluoroaromatic compounds. However, at the beginning of the work described in this Paper, only one type of free-radical reaction with polyfluoroarenes had been reported, namely the photochemical addition of chlorine to hexa- or penta-fluorobenzene to give the corresponding hexachloropolyfluorocyclohexanes.[2] Very recently, reactions have been described of hexafluorobenzene with phenyl or substituted phenyl radicals to yield pentafluorobiphenyls.[3] Further examples of the homolytic displacement of fluorine from the aromatic ring are now provided by the reactions of trichlorosilyl or trimethylsilyl radicals with hexafluorobenzene, which provide direct routes to polyfluoroaryl derivatives of silicon. The only compound of this class to be described hitherto is tetrakispentafluorophenylsilane, which results from the reaction of silicon tetrachloride with pentafluorophenylmagnesium bromide.[4]

*Reaction with Trichlorosilane.*—Prolonged ultraviolet irradiation of equimolar proportions of hexafluorobenzene and trichlorosilane gives traces of hydrogen (<1%), hydrogen chloride [94% based on trichlorosilane consumed (96%)], dichlorofluoro(pentafluorophenyl)silane, $C_6F_5{\cdot}SiFCl_2$ [61% based on hexafluorobenzene consumed (70%)], and an oily residue. The infrared (i.r.) spectrum of the compound $C_6F_5{\cdot}SiFCl_2$ reveals the characteristic polyfluoroarene bands[5] at 1472, 1516, and 1642 cm.$^{-1}$, and in particular shows the absence of olefinic absorption in the 1700—1800-cm.$^{-1}$ region. Hydrolysis of the silane derivative with water liberates chloride and fluoride ions and gives the white solid polysiloxane, which is decomposed by aqueous sodium hydroxide to give pentafluorobenzene:

$$C_6F_5{\cdot}SiFCl_2 \xrightarrow{H_2O} [C_6F_5{\cdot}SiO_{1{\cdot}5}]_n \xrightarrow[100^\circ]{\text{NaOH aq.}} C_6F_5H\ (74\%)$$

The high-boiling residue from the reaction of hexafluorobenzene with trichlorosilane is obtained in about 25 moles % yield, based on hexafluorobenzene consumed. Its i.r. spectrum shows strong fluoroaromatic bands in the 1450—1650-cm.$^{-1}$ region, but weak olefinic absorption at 1730 cm.$^{-1}$ is also present. The material distils over a wide temperature range, but it cannot easily be separated into individual components by fractional distillation or by analytical gas–liquid chromatography (g.l.c.). Hydrolysis of the mixture with aqueous sodium hydroxide at 100° gives a mixture of polyfluorobenzenes (*ca.* 60 moles % yield), which is shown by g.l.c. to consist of pentafluorobenzene (50%), 1,2,3,5-tetrafluorobenzene (25%), 1,2,4,5-tetrafluorobenzene (20%), and 1,2,3,4-tetrafluorobenzene

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[1] Part VI, J. M. Birchall, T. Clarke, and R. N. Haszeldine, *J.*, 1962, 4977.

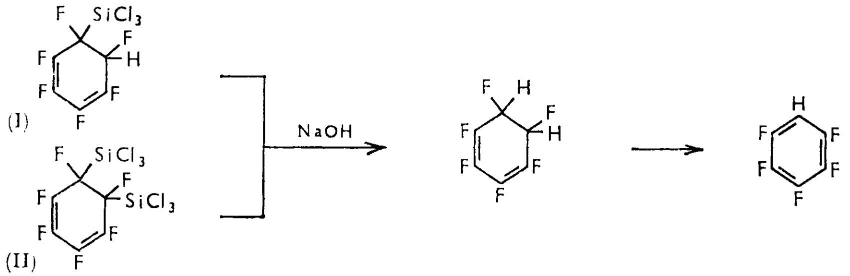
[2] J. A. Godsell, M. Stacey, and J. C. Tatlow, *Nature*, 1956, **178**, 199; E. Nield, R. Stephens, and J. C. Tatlow, *J.*, 1959, 166.

[3] P. A. Claret, J. Coulson, and G. H. Williams, *Chem. and Ind.*, 1965, 228.

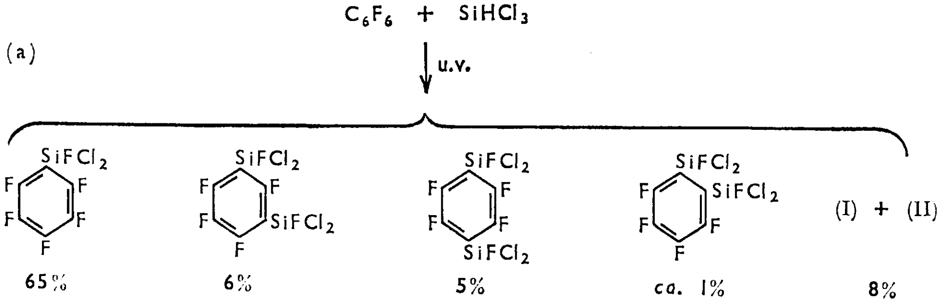
[4] L. A. Wall, R. E. Donadio, and W. J. Pummer, *J. Amer. Chem. Soc.*, 1960, **82**, 4846.

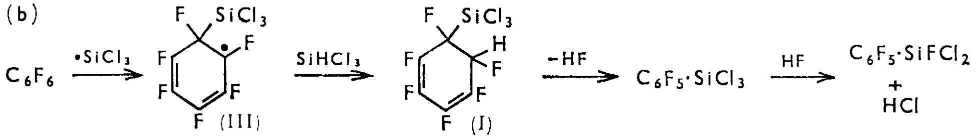
[5] Cf. earlier Papers in this Series, particularly J. M. Birchall and R. N. Haszeldine, *J.*, 1959, 13, and references cited therein.

(5%). The tetrafluorobenzenes presumably arise by the hydrolysis of compounds of the type $C_6F_4(SiFCl_2)_2$, formed by the attack of trichlorosilyl radicals on the principal product from the reaction between hexafluorobenzene and trichlorosilane. Some of the pentafluorobenzene undoubtedly arises from hydrolysis of the compound $C_6F_5{\cdot}SiFCl_2$ present as impurity in the high-boiling fraction, but the i.r. spectrum of the last material shows that there is insufficient $C_6F_5{\cdot}SiFCl_2$ present for it to be the only source of pentafluorobenzene in the hydrolysate. The remainder may be formed by the hydrolysis of compounds (I) and (II) (or their 1,4-isomers), the probable presence of at least one of which in the high-boiling material is indicated by the olefinic i.r. absorption.



The maximum possible yield of such cyclohexadienylsilanes from the reaction of hexafluorobenzene with trichlorosilane is limited by the high recovery of hydrogen chloride and, in the case of (II), by the failure to detect more than traces of hydrogen among the products. With the assumption that the composition of the high-boiling material is directly related to the composition of the mixture of polyfluorobenzenes obtained as above, the course of the photochemical reaction may be summarised as shown (*a*) (yields based on hexafluorobenzene consumed; remaining 15% attributed to losses during work-up and to tar formation).





Formation of dichlorofluoro(pentafluorophenyl)silane from hexafluorobenzene by the route indicated (*b*) would involve formation of the adduct (I), which is probably present among the final products of the reaction; silyl-radical addition to the ring would be formally analogous to the established homolytic addition of trichlorosilane to fluoro-olefins.[6] However, the liberation of hydrogen fluoride during the course of the reaction in a silica vessel would undoubtedly lead to considerable etching and to the production of substantial

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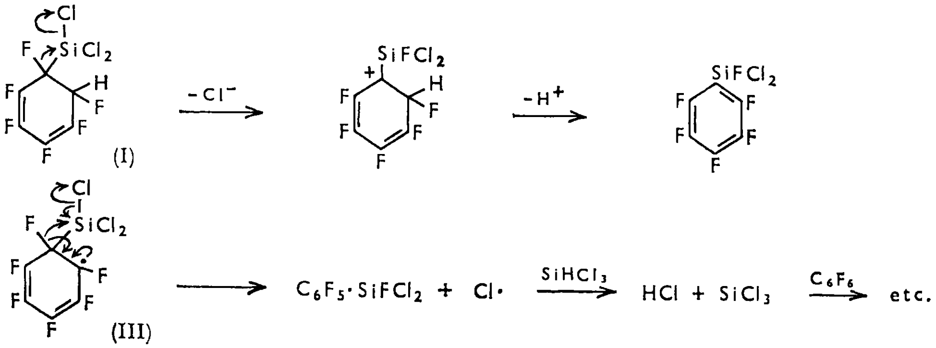
[6] R. N. Haszeldine and J. C. Young, *J.*, 1960, 4503, and earlier Papers in the Series.

quantities of silicon tetrafluoride and trifluorosilane, none of which is observed. Formation of dichlorofluoro(pentafluorophenyl)silane by decomposition of the diene (I) must thus involve internal nucleophilic attack by fluoride on silicon, as shown below. It seems more probable that the main path of the reaction does not proceed through the diene (I), but that rearrangement of the σ-complex (III) leads directly to the regeneration of the aromatic ring with elimination of a chlorine atom and propagation of the chain.



*Reaction with Trimethylsilane.*—The photochemical reaction between hexafluorobenzene and trimethylsilane follows a different path from that with trichlorosilane. Irradiation of an equimolar mixture of the reactants leads to the recovery of half of the hexafluorobenzene, and a main reaction as follows:

$$C_6F_6 + 2Me_3SiH \xrightarrow{\text{u.v.}} C_6F_5{\cdot}SiMe_3\ (53\%) + Me_3SiF\ (56\%) + H_2\ (46\%)$$

accompanied by formation of a high-boiling liquid mixture and a tar. The structure of the main organic product, chromatographically pure trimethylpentafluorophenylsilane, is confirmed by elemental analysis, i.r. spectroscopy, hydrolysis, and independent synthesis from pentafluorophenylmagnesium bromide and chlorotrimethylsilane. The i.r. spectrum shows fluoroaromatic ring absorption at 1453, 1511, and 1637 cm.$^{-1}$, and C–F absorption at 970 cm.$^{-1}$. Several bands at positions which have been assigned to Si–C vibrations in compounds containing the $Me_3Si$ group[7] are also present, notably at 769, 868, and 1252 cm.$^{-1}$ (cf. $PhSiMe_3$,[8] 767, 841, and 1249 cm.$^{-1}$).

Nucleophilic aryl–silicon cleavage, as observed on alkaline hydrolysis of trimethylpentafluorophenylsilane in aqueous dioxan at 90°:

$$2C_6F_5{\cdot}SiMe_3 + H_2O \longrightarrow 2C_6F_5H\ (75\%) + (Me_3Si)_2O\ (75\%)$$

is not usually accomplished easily, although it has been noted that the presence of electron-withdrawing substituents in an aryl group greatly facilitates its displacement. Thus, trimethylphenylsilane is not detectably cleaved by potassium hydroxide in refluxing aqueous acetone, but benzotrifluoride is obtained in 51% yield from triphenyl-(*m*-trifluoromethylphenyl)silane by alkaline hydrolysis in aqueous ethanol–dioxan.[9]

The high-boiling mixture from the reaction of hexafluorobenzene with trimethylsilane distils over a wide temperature range and comprises about 42% by weight of the consumed reactants. Its i.r. spectrum shows medium-strength olefinic absorptions at 1664, 1730, and 1757 cm.$^{-1}$, and no strong aromatic bands in the 1450—1550-cm.$^{-1}$ region. Alkaline hydrolysis in aqueous dioxan gives only two major products, hexamethyldisiloxane and pentafluorobenzene, and small amounts of an unidentified compound (not a tetrafluorobenzene). The i.r. spectrum of the original mixture, and the absence of tetrafluorobenzenes from the hydrolysate, indicate that the displacement of a second fluorine atom during the

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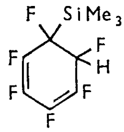
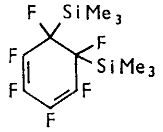
[7] L. J. Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen and Co., London, 1958, 2nd edn., p. 335.

[8] C. C. Cerato, J. L. Lauer, and H. C. Beachell, *J. Chem. Phys.*, 1954, **22**, 1.

[9] H. Gilman, A. G. Brook, and L. S. Miller, *J. Amer. Chem. Soc.*, 1953, **75**, 4531.

photolysis, to give compounds of the type $C_6F_4(SiMe_3)_2$, has not occurred, perhaps because the reactant ratio was such that half of the hexafluorobenzene did not react. The high-boiling fraction thus contains substantial amounts of the dienes (IV) and (V) and their 1,4-isomers.


(IV)

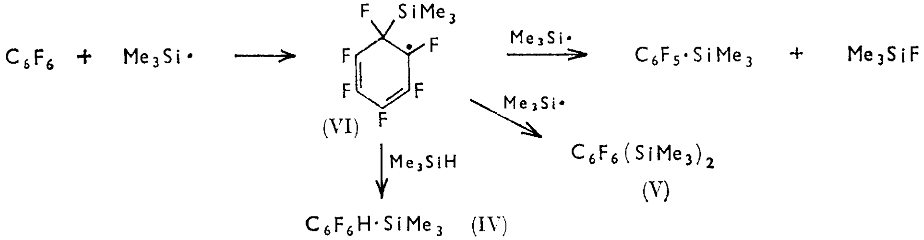

(V)

This deduction is in accord with the formation of fluoride ion during the hydrolysis, since both (IV) and (V) would be expected to react readily with base.

Since silicon tetrafluoride is not formed, even in trace quantities, it is improbable that the main path of the reaction, to give the compound $C_6F_5 \cdot SiMe_3$, proceeds through dehydrofluorination of the simple adduct (IV). The elimination of fluorotrimethylsilane from the diene (V) also seems unlikely, but by no means impossible, under the conditions employed. Although a number of possible routes to trimethylpentafluorophenylsilane may be written, the most feasible involves formation of the σ-complex (VI), from which a fluorine atom is removed by a second trimethylsilyl radical.

$$Me_3SiH \xrightarrow{u.v.} Me_3Si\cdot + H\cdot$$

$$H\cdot + Me_3SiH \longrightarrow Me_3Si\cdot + H_2$$



Removal of the fluorine atom from the complex (VI) by another radical may be compared with the favoured process for the removal of a hydrogen atom from the σ-complexes formed in the homolytic substitution reactions of benzene itself.[10]

## EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer model 21 instrument. G.l.c. was carried out on a Perkin-Elmer model 154B or 116 instrument, with a glass column (2 m. × 4 mm. i.d.) packed with 30% by weight of the stationary phase of trixylenyl phosphate (except when otherwise stated) on 80-mesh Celite. Molecular weights were determined by Regnault's method.

*Reaction of Hexafluorobenzene with Trichlorosilane.*—Hexafluorobenzene (20·0 g., 0·108 mole) and trichlorosilane (14·0 g., 0·103 mole), sealed *in vacuo* in a 300-ml. silica tube, were shaken continuously and irradiated for 240 hr. by ultraviolet light from a Hanovia 500-w mercury discharge tube. A trace of non-condensable gas, presumed to be hydrogen (*ca.* 0·7 mmole, <1%), was formed, and products which were volatile at room temperature were separated by fractional condensation *in vacuo* into hexafluorobenzene (5·0 g.), trichlorosilane (0·54 g., 4% recovery) (Found: *M*, 137. Calc. for $SiHCl_3$: *M*, 135·5), and hydrogen chloride (3·40 g., 94% based on $SiHCl_3$ consumed) (Found: *M*, 36·9). The hexafluorobenzene was added to the liquid products from the reaction, which were washed from the tube with dry light petroleum (5 ml.; b. p. <40°) in an atmosphere of nitrogen. Distillation through a vacuum-jacketed Vigreux column (35 × 1 cm.) gave hexafluorobenzene (6·0 g., 30% recovery), b. p. 81°, identified by i.r. spectroscopy, *dichlorofluoro(pentafluorophenyl)silane* (13·0 g., 61% based on $C_6F_6$ consumed) (Found: C, 25·0; Cl, 24·9; F, 40·4. $C_6Cl_2F_6Si$ requires C, 25·1; Cl, 25·0; F, 40·0%), b. p. 83°/57 mm., and an oily brown residue (6·0 g.). The i.r.

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[10] G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, London, 1960, p. 50.

spectrum of the silane shows strong bands at 728, 756, 852, 926, 974, 1096, 1300, 1389, 1472, 1516, and 1642 cm.$^{-1}$.

The crude residues (18 g.) from three experiments were combined and distilled under reduced pressure through the 35 cm. Vigreux column. No definite fraction could be obtained, and distillation was stopped at 150°/1 mm., when about 80% of the material had distilled. The distillate and residue were combined and heated under reflux with aqueous 20% sodium hydroxide (150 ml.) for 3 hr. The mixture was steam-distilled, and the steam-distillate was dried ($P_4O_{10}$) to give a colourless mobile liquid (5 g.), which was shown to contain four components by g.l.c. at 90°. Samples of the first three were collected and identified by i.r. spectroscopy as 1,2,4,5-tetrafluorobenzene (*ca.* 20% of the mixture, 1·0 g.), pentafluorobenzene (*ca.* 50%, 2·5 g.) (Found: *M*, 169. Calc. for $C_6F_5H$: *M*, 168), and 1,2,3,5-tetrafluorobenzene (*ca.* 25%, 1·25 g.), respectively. The amounts of these compounds in the mixture were determined by subsequent comparison of the chromatogram against that of a standard mixture. The fourth component (*ca.* 5%, 0·25 g.) could not be isolated because of the small amount present, but its retention time was identical with that of 1,2,3,4-tetrafluorobenzene. The dark brown aqueous residue from the hydrolysis yielded no further products when it was extracted with ether, both before and after acidification.

*Hydrolysis of Dichlorofluoro(pentafluorophenyl)silane.*—The silane (5·0 g.) was added slowly to well-stirred ice-cold water (100 ml.), and the white solid polysiloxane formed was washed with water and then heated under reflux with aqueous 20% sodium hydroxide (100 ml.) for 3 hr. The mixture was steam-distilled, and the organic distillate was transferred directly to a high-vacuum apparatus and dried ($P_4O_{10}$), to give chromatographically pure pentafluorobenzene (2·2 g., 74%), identified by its molecular weight and i.r. spectrum. The aqueous phase from the first stage of the hydrolysis contained chloride and fluoride ions.

*Reaction of Hexafluorobenzene with Trimethylsilane.*—Hexafluorobenzene (18·6 g., 0·10 mole) and trimethylsilane (7·4 g., 0·10 mole) were irradiated for 240 hr. in a 300-ml. silica tube under conditions identical with those employed for the reaction with trichlorosilane. The tube was cooled to −196°, opened, and the non-condensable gas, which passed through four traps at −196°, was adsorbed onto charcoal at −196°, and identified as hydrogen (0·023 mole) (Found: *M*, 1·8). Fractional condensation of the remaining volatile products *in vacuo* gave hexafluorobenzene and fluorotrimethylsilane (2·58 g., 0·028 mole) (Found: *M*, 90. Calc. for $C_3H_9FSi$: *M*, 92), identified by i.r. spectroscopy. The hexafluorobenzene was combined with the liquid products, which were distilled through the 35-cm. Vigreux column to give hexafluorobenzene (9·1 g., 49%), b. p. 80—82°, shown to be at least 95% pure by g.l.c. and i.r. spectroscopy, a fraction (7·3 g.) of b. p. 93°/57 mm., and a residue (7·0 g.). The fraction boiling at 93°/57 mm. was redistilled at atmospheric pressure and gave chromatographically pure (Silicone "MS 550," at 175°) *trimethylpentafluorophenylsilane* (6·5 g., 53% based on $C_6F_6$ consumed) (Found: C, 44·9; H, 3·8. $C_9H_9F_5Si$ requires C, 45·0; H, 3·8%), b. p. 170°. The i.r. spectrum of this compound shows bands at 697w, 730w, 769m, 778w, 812s, 847vs, 868s, 970vs, 1085s, 1100w, 1252s, 1282m, 1368w, 1408w, 1453vs, 1511s, 1637m, and 2933w cm.$^{-1}$.

The residues from this experiment began to distil at 100°/4 mm., and the distillation was stopped at 149°/0·1 mm., when most of the material (6·1 g.) had distilled, but no discrete fraction had been obtained. The accumulated, undistilled, residues from three experiments (18 g.) were dissolved in dioxan (50 ml.) and heated under reflux with aqueous 20% sodium hydroxide (100 ml.) for 3 hr. Steam-distillation then afforded an oil (5 g.), which was dried ($MgSO_4$) and shown to contain three components by g.l.c. at 100°. The two major components were isolated by g.l.c. and identified by i.r. spectroscopy and molecular-weight measurements as hexamethyldisiloxane (*ca.* 57% of the mixture, 2·9 g.) and pentafluorobenzene (*ca.* 29%, 1·5 g.). The third component (*ca.* 14%) was not isolated and remained unidentified.

*Hydrolysis of Trimethylpentafluorophenylsilane.*—The silane (2·0 g., 0·008 mole), aqueous 20% sodium hydroxide (20 ml.), and dioxan (5 ml.) were heated at 90° for 5 hr. in a 100-ml. sealed Pyrex tube in the absence of air. The volatile products were dried by fractional condensation *in vacuo* and yielded a single fraction (1·7 g.); this was separated by g.l.c. at 100° into pentafluorobenzene (66 moles % of the fraction, 75% yield) and hexamethyldisiloxane (34% of the fraction, 75% yield), identified by i.r. spectroscopy. Extraction of the acidified aqueous phase from the hydrolysis yields no further material, and the reason for the comparatively low recovery of the products from this, and from the related hydrolyses described in this Paper, is not at present clear.

*Trimethylpentafluorophenylsilane from Pentafluorophenylmagnesium Bromide.*—Chlorotrimethylsilane (4·0 g., 0·035 mole) in ether (20 ml.) was heated under reflux with ethereal pentafluorophenylmagnesium bromide [from bromopentafluorobenzene (7·5 g., 0·030 mole), magnesium turnings (0·75 g., 0·031 g.-atom), and ether (50 ml.)]. Removal of the solvent under reduced pressure, and distillation of the residue, then gave trimethylpentafluorophenylsilane (2·3 g., 33% based on $C_6F_5Br$) (Found: C, 44·6; H, 3·8. Calc. for $C_9H_9F_5Si$: C, 45·0; H, 3·8%), b. p. 170—172°. The i.r. spectrum was identical with that of the sample described above.

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