Some Pentafluorophenyl Tin Compounds

By J. M. Holmes, R. D. Peacock, and J. C. Tatlow

The action of pentafluorophenylmagnesium bromide on tin(IV) chloride yields tetrakispentafluorophenyltin and pentafluorophenyltin chlorides, whose hydrolysis products are described.

IN a preliminary Communication[1] we described the preparation of tetrakispentafluorophenyltin and the halides $(C_6F_5)_3SnCl$ and $(C_6F_5)_2SnCl$. Further publications have since appeared in the same field.[2-4] We now report more fully on the pentafluorophenyltin compounds and on the hydrolysis products of the halides.

Tetrakispentafluorophenyltin (I) is a white crystalline solid, m. p. 218—219°, which, unlike its hydrocarbon analogue, dissolves in diethyl ether. The compound is unaffected by water, by chlorine gas at 20° and 8 atm., even under the influence of ultraviolet radiation, by hydrogen bromide at 20°, by liquid bromine at 20°, by bromine in carbon tetrachloride solution, by boron trifluoride at 220°, and by mercury(II) dichloride in boiling methanolic solution. However, compound (I)

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[1] J. M. Holmes, R. D. Peacock, and J. C. Tatlow, *Proc. Chem. Soc.*, 1963, 108.

[2] R. D. Chambers and T. Chivers, *J. Chem. Soc.*, 1964, 4782.

[3] R. D. Chambers and T. Chivers, *Proc. Chem. Soc.*, 1963, 208.

[4] A. G. Massey, E. W. Randall, and D. Shaw, *Chem. and Ind.*, 1963, 1244.

reacts with sulphur tetrafluoride to give[5] the fluoride $(C_6F_5)_3SnF$. With 8-hydroxyquinoline (oxine) the tetrakis-compound (I) breaks down to bispentafluorophenyltin di-(8-hydroxyquinolate) (II), which is a yellow crystalline solid, m. p. 277° (decomp.) (cf. diphenyltin dioxinate,[6] m. p. 231—233°). The rearrangement reaction of compound (I) with tin(IV) chloride goes only slowly at 140°, in contrast to the corresponding hydrocarbon reaction.[7]

Pentafluorophenyltin halides have been obtained by the action of an excess of tin(IV) chloride on pentafluorophenylmagnesium bromide. The dichloro- and trichloro-compounds result when the monochloro-compound is treated with tin(IV) chloride, and the dichloro- and impure dibromo-compounds result when dimethylbispentafluorophenyltin is treated with the tin(IV) halide. Recent studies[2] have shown that the action of hydrogen chloride on unsymmetrical *p*-tolylpentafluorophenyltin compounds specifically cleaves the hydrocarbon group, yielding the pentafluorophenyltin halide. *o*-Tolyl derivatives appear to behave similarly.

The reactivity of the halides increases with the number of halogen atoms. All are decomposed by strong alkali to pentafluorobenzene and stannic oxide, but, under controlled conditions, hydrolysis may yield fluoroaryl oxides and hydroxides. With oxine they give the oxinate (II), and with tetramethylammonium chloride is formed tetramethylammonium hexachlorostannate(IV).

$$(C_6F_5)Sn\ (I) \qquad (C_6F_5)_5Sn(OX)_2\ (II) \qquad C_6F_5Sn{\cdot}O{\cdot}OH\ (III)$$

Pentafluorophenyltin trichloride, which fumes in moist air,[2] hydrolyses in water to give pentafluorophenylstannonic acid (III), a white solid which dissolves in organic solvents.

Treatment of trispentafluorophenyltin chloride in di-isopropyl ether with 0·05N-sodium hydroxide gives trispentafluorophenyltin hydroxide (IV) as a white residue. This melts at 150° if heated quickly, but decomposes at this temperature, one of the products being the tetrakis-compound (I). When the hydroxide is heated *in vacuo* it loses water to form bis(trispentafluorophenyltin) oxide (V), which in turn dismutates to bispentafluorophenyltin oxide (VI) and tetrakispentafluorophenyltin. If the water is not removed sufficiently quickly a little pentafluorobenzene also

$$(C_6F_5)_3SnOH\ (IV) \xrightarrow[\text{1 hr.}]{100°/2\text{ cm}} H_2O + [(C_6F_5)_3Sn]_2O\ (V)$$

$$(C_6F_5)_3SnOH \xrightarrow[\text{70 hr.}]{100°/10^{-3}\text{ mm}} H_2O + (C_6F_5)_2SnO\ (VI) + C_6F_5H + (C_6F_5)_4Sn$$

appears. The hydroxide (IV) gives the monobromide with hydrobromic acid, but does not combine with hydriodic or hydrofluoric acid. With oxine it gives the dioxinate (II).

Bis(trispentafluorophenyltin) oxide (V), formed from the hydroxide (IV), is chemically similar to the hydroxide but has a characteristic Guinier *X*-ray powder pattern. An earlier claim to this compound[2] does not clearly distinguish it from the hydroxide (IV).

The hydroxide (IV) and the oxides have characteristic infrared spectra. The absorption frequencies expected for the pentafluorophenyl group[2] are present, and the hydroxide shows an absorption at 3600 cm.$^{-1}$ associated with the Sn–OH group.[8,9] Other frequencies also appear; some of these must be associated with the Sn–O grouping but insufficient information is available to assign them with certainty.

DISCUSSION

The equilibrium in the reaction between the perfluoro-Grignard reagent and an excess of tin(IV) chloride is attained only slowly, and the fully substituted $(C_6F_5)_4Sn$ is formed preferentially; this is like the corresponding silicon case,[10] in which it has been suggested that the remaining chlorine atoms become activated after the first has been replaced.

Measurements of the recoil-less emission and absorption for γ-rays (Mössbauer effect) in tetraphenyltin, tetrakispentafluorophenyltin, pentafluorophenyltin halides, and mixed aryl-fluoroaryltin compounds indicate that the chemical shift of the C_6F_5 group, which is related to the electronegativity, is close to that of bromide.[11] More surprisingly, the chemical shift of the C_6F_5 and C_6H_5 groups are very close to one another, both in symmetrical and unsymmetrical compounds;[11] at first sight this result is anomalous for C_6H_5. Proton magnetic resonance studies have indicated[4] that the electron-withdrawing sequence is $Cl > C_6F_5 > Br$.

Tetrakispentafluorophenyltin shows little depression of melting point when mixed with its hydrocarbon analogue, although the individual unsymmetrical compounds melt much lower. This probably indicates similar structures and lattice energies for the two compounds. However, it has not proved possible to index the crystallographic data for tetrakispentafluorophenyltin by analogy with the known unit cell of tetraphenyltin.[12] A mixture of triphenyltin chloride and its fluoro-analogue similarly shows no depression of melting point.

The pentafluorophenyltin hydroxide and oxides hydrolyse completely to tin(IV) oxide when heated with water vapour, and have a limited thermal stability. Only the oxide (V) is monomeric. The hydroxide (IV) is dimeric in acetone; similar compounds, involving

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[8] R. L. Williams and R. J. Pace, *J. Chem. Soc.*, 1957, 4143.

[9] R. C. Poller, *J. Chem. Soc.*, 1963, 708; *J. Inorg. Nuclear Chem.*, 1962, **24**, 593; B. G. Kushlefsky, I. L. Simons, and A. Ross, *Inorg. Chem.*, 1963, **2**, 187; E. Frieke and H. Kelker, *Z. analyt. Chem.*, 1963, **192**, 267.

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

[11] M. Cordey-Hayes, *J. Inorg. Nuclear Chem.*, 1964, **26**, 2306; private communication, 1964.

[12] G. S. Zhadanov and I. G. Ismailzade, *Zhur. fiz. Khim.*, 1950, **24**, 1945 (*Chem. Abs.*, 1951, **45**, 4112).

5-co-ordinated tin, have been invoked as intermediates during the hydrolysis of the phenyltin halides.[13]

EXPERIMENTAL

Pentafluorobromobenzene was made by the procedure devised in the Birmingham University laboratories,[14] but was later obtained from the Imperial Smelting Corporation. All reactions involving pentafluorophenylmagnesium bromide [15] were carried out under dry nitrogen. Boiling points and melting points are uncorrected.

Fully Substituted Tin(IV) *Compounds*.—From tin(IV) chloride and the Grignard reagent, tetrakispentafluorophenyltin was obtained (Found: C, 37·0; H, 0·0; F, 48·2; Sn, 14·8. Calc. for $C_{24}F_{20}Sn$: C, 37·0; H, 0·0; F, 48·2; Sn, 15·1%), m. p. 218—219° (lit.,[1,4] 221°). From the appropriate tin(IV) halogen compound and the Grignard reagent the following were prepared: (*a*) dimethylbispentafluorophenyltin (Found: C, 35·1; H, 1·4. Calc. for $C_{14}H_6F_{10}Sn$: C, 34·8; H, 1·3%), b. p. 94—96°/1·7 mm., n_D^{20} 1·4970 (lit.,[1] 94—96°/1·7 mm., lit.,[2] 74—76°/10^{-2} mm.); (*b*) diphenylbispentafluorophenyltin (Found: C, 46·8; H, 1·5; F, 31·4. Calc. for $C_{24}H_{10}F_{10}Sn$: C, 47·4; H, 1·6; F, 31·3%), m. p. 78° (lit.,[2] 85°); (*c*) phenyltrispentafluorophenyltin (Found: C, 42·3; H, 1·0; F, 40·7; Sn, 17·7. Calc. for $C_{24}H_5F_{15}Sn$: C, 41·2; H, 0·7; F, 40·9; Sn, 17·1%), m. p. 100—102° (lit.,[2] 95—96°); (*d*) *di-*o*-tolylbispentafluorophenyltin* (Found: C, 47·8; H, 1·8; F, 30·6. $C_{26}H_{14}F_{10}Sn$ requires C, 49·1; H, 2·2; F, 29·9%), m. p. 174°.

Preparation of Pentafluorophenyltin Halides from Tin(IV) *Chloride and the Grignard Reagent*.—Tin(IV) chloride (3·8 g., 176 mmoles) in pentane (30 ml.) was added to the Grignard reagent (437 mmoles) at 20° and heated under reflux for 10 hr. The solvent-free products were sublimed through a temperature-graded column, which was a horizontal glass tube (3·1 cm. diameter) separated by constrictions into several sections (each 17 cm. long). Initially the product was held in a bulb at one end of the tube, which was maintained at 10^{-3} mm. The bulb and the tube were heated electrically with fibre glass tapes arranged to produce a regular fall of temperature along the column, with the hot end at 130° and the cold end at the ambient temperature. After 80 hr. the content of the zone at 70—80° was crystallised (methanol, 100 ml.) to give compound (I) (8·0 g.) and a white crystalline solid (18·0 g.) which contained solvent. A portion of the solid, recrystallised from perfluoro-*p*-xylene (4 ml.) gave trispentafluorophenyltin chloride (Found: C, 32·3; H, 0·0; Cl, 5·5; F, 42·9; Sn, 18·8. Calc. for $C_{18}ClF_{15}Sn$: C, 33·0; H, 0·0; Cl, 5·4; F, 43·5; Sn, 18·2%), m. p. 103—104° (lit.,[1] 106°; lit.,[2] 108—109). The condensate from tube sections at 50—20° was distilled to give *bispentafluorophenyltindichloride* (Found: Cl, 13·8%; *M*, 557. $C_{12}Cl_2F_{10}Sn$ requires Cl, 13·6%; *M*, 523), b. p. 61°/0·15 mm.; 113°/3 mm.; d_4^{20} 2·4.

Rearrangement Reactions (*in Sealed, Evacuated Tubes*).—The compound (I) was recovered unchanged after being heated with tin(IV) chloride at 150° for 7 hr. Tin(IV) chloride and (I) (1·24 g., 1·5 mmoles), after 7 days at 160° followed by crystallisation from ether, yielded trispentafluorophenyltin chloride (0·5 g.), m. p. 104°. Tin(IV) chloride (2·2 g., 7·6 mmoles) and (I) (2·2 g., 2·8 mmoles), heated for 11 weeks at 140° gave impure pentafluorophenyltin trichloride (Found: C, 20·4; H, 0·0; Cl, 25·8; F, 24·6. Calc. for $C_6Cl_3F_5Sn$: C, 18·4; H, 0·0; Cl, 27·2; F, 24·2%).

Trispentafluorophenyltin chloride (2·7 g., 4·12 mmoles) and tin(IV) chloride (0·6 g., 2·3 mmoles), heated at 150° for 5 weeks, gave, after vacuum distillation, impure bispentafluorophenyltin dichloride (Found: Cl, 11·0; F, 38·1; Calc. for $C_{12}Cl_2F_{10}Sn$: Cl, 13·6; F, 36·3%). The monochloride, heated with excess of tin(IV) chloride for 4 weeks at 120°, gave pentafluorophenyltin trichloride (5·3 g., 13·5 mmoles) (Found: Cl, 28·8. Calc. for $C_6Cl_3F_5Sn$: Cl, 27·2%), b. p. 120—122°/16 mm. (lit.,[2] 54—56°/0·02 mm.).

Dimethylbispentafluorophenyltin (6·0 g., 12·5 mmoles) and tin(IV) chloride (3·25 g., 12·5 mmoles), heated at 150° for 3 days, gave (*a*) dimethyltin dichloride, identified by its m. p. and infrared spectrum, and (*b*) impure bispentafluorophenyltin dichloride (1·4 g., 35%) (Found: C, 25·9; H, 0·1; Cl, 13·9; F, 39·0. Calc. for $C_{12}Cl_2F_{10}Sn$: C, 27·5; H, 0·0; Cl, 13·6; 36·6%), b. p. 130—140°/2 mm. Similarly, bispentafluorophenyltin dibromide (containing 20% dimethyltin dibromide) was prepared (Found: C, 19·4; H, 0·3; F, 27·5; Br, 40·0. Calc. for $C_{12}BrF_{10}Sn$: C, 23·5; H, 0·0; F, 31·0; Br, 26·1%), b. p. 68°/0·2 mm.

Reactions Involving the Sn–O *Group*.—*Trispentafluorophenyltin hydroxide*. Trispentafluorophenyltin chloride (6·97 g., 10·6 mmoles) in di-isopropyl ether (50 ml.) was shaken with 0·05N-sodium hydroxide (213 ml., 10·6 mmoles). Evaporation of the ether layer yielded a white solid; a portion, crystallised from di-isopropyl ether and dried over silica gel, yielded *trispentafluorophenyltin hydroxide* (IV) (Found: C, 33·7; H, 0·3; F, 45·6; Sn, 18·6%; *M*, 1150. $C_{36}H_2F_{30}O_2Sn_2$ requires C, 34·0; H, 0·2; F, 45·6; Sn, 18·6%; *M*, 1264), $\nu_{max.}$ *3650*, 1650, 1520, 1485, 1460sh, 1380, 1365sh, 1340, 1290, 1235, *1150*, 1100sh, 1090, 1075sh, 1030sh, 1015, 980sh, 970, 860, 845, 810, 747, 720, 615, 585, 493, *445* cm.$^{-1}$, where characteristic absorptions are in italics. The hydroxide (IV) gave a characteristic Guinier *X*-ray powder photograph. A sample, heated slowly to 300°, did not melt, but another, heated rapidly at 150°, melted and resolidified after 15 min. at 150°. A sublimate in the cool part of the capillary was identified as compound (I) by a mixed melting point and by a Guinier *X*-ray powder photograph.

Bis(*trispentafluorophenyltin*) *oxide*. Trispentafluorophenyltin hydroxide, heated at 100°/2 cm. for 1 hr., gave *bis*(*trispentafluorophenyltin*) *oxide* (Found: C, 33·7; H, 0·2. $C_{36}F_{30}Sn_2O$ requires C, 33·4; H, 0·0%), $\nu_{max.}$ 1650, 1520, 1485, 1460sh, 1380, 1365, 1285, 1230, 1145, 1100, 1080, 1030, 1018, 975, *905*, 840, 810, 745, 718, 610, 584, 490 cm.$^{-1}$. The compound gave a characteristic Guinier photograph.

Bispentafluorophenyltin oxide. The hydroxide (IV) was heated at 100°/10^{-3} mm. for 70 hr. Three fractions were separated: (*a*) a solid residue, (*b*) a crystalline sublimate, and (*c*) a gaseous fraction which condensed at −187°. The first fraction did not give a Guinier *X*-ray powder photograph, did not melt below 300°, and did not dissolve in acetone. This was (polymeric) *bispentafluorophenyltin oxide* (Found: C, 31·8; H, 0·1; F, 40·5; Sn, 26·0. $C_{12}F_{10}SnO$ requires C, 30·7; H, 0·0; F, 40·5; Sn, 25·3%), $\nu_{max.}$ 1650, 1582, 1485, 1400sh, 1380, 1365sh, 1285, 1230, 1145, 1095, 1080sh, 1025, 1010, 980sh, 970, 905, 805, 750sh, 745, 720, 612, *570*, 493, *450* cm.$^{-1}$. Fraction (*b*), m. p. 218°,

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[15] E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.* 1959, 166.

was identified as (I) by its Guinier *X*-ray powder photograph. Fraction (*c*) was shown by mass spectrometry to contain pentafluorobenzene and water.

Hydrolysis of Bispentafluorophenyltin Dichloride.—A solution in acetone of the dichloride (1·31 g.) was shaken with water (5 ml.) at 20°. The white precipitate (1·0 g., 86%), was dried at 20° over silica gel [Found: C, 28·8; H, 1·3; F, 35·9; Sn, 25·5%; *M* (in acetone), 1785]. The material had characteristic absorption frequencies at 571 and 450 cm.$^{-1}$. We are grateful to the referees for pointing out that this material resembles the compounds $R_4Sn_2Cl_2O$ recently reported;[16] in the absence in a complete analysis no certain claim to identity can be made. Hydrolysis of the dichloride at 100° yielded a product, insoluble in acetone, which contained C_6F_5 groups, but this was not obtained in sufficient quantity to be fully identified. The material had characteristic absorption frequencies at 571 and 553 cm.$^{-1}$.

Bispentafluorophenyltin Dioxinate.—A mixture of the tetrakis-compund (I) and an excess of oxine in ethanol was heated under reflux for 12 hr. The solution deposited yellow crystals of the *dioxinate*, m. p. 277° (decomp.) (Found: C, 48·7; H, 1·7; N, 3·8. $C_{30}H_{12}F_{10}N_2O_2Sn$ requires C, 48·6; H, 1·6; N, 3·8%), $\nu_{max.}$ 1650, 1630, 1580, 1525, 1505, 1485, 1460sh, 1430sh, 1395sh, 1380, 1330, 1285, 1270, 1240, 1230, 1180, 1130, 1108, 1080, 1075sh, 1055sh, 1030, 1010, 965, 900, 845sh, 840, 809, 790, 760sh, 755, 748sh, 744, 720, 710 cm.$^{-1}$. The dioxinate was obtained similarly from trispentafluorophenyltin chloride, from the hydroxide (IV), and from bispentafluorophenyltin dichloride; the compound was identified by its m. p. and Guinier *X*-ray powder pattern.

Reactions of the Monochloride and Dichloride with Tetramethylammonium Chloride.—The product in each case was tetramethylammonium hexachlorostannate, identified by its characteristic *X*-ray powder photograph.

Reaction of Trispentafluorophenyltin Hydroxide with Hydrogen Bromide.—The hydroxide (1·5 g.) was dissolved in diethyl ether, and the solution was shaken with 3N-hydrobromic acid (10 ml.). The solid obtained from evaporation of the ethereal layer was sublimed at 10^{-3} mm.: recrystallisation from perfluoro-*p*-xylene yielded *trispentafluorophenyltin bromide* (0·4 g.), m. p. 107—108° (Found: C, 31·6; H, 0·0; Br, 11·4; F, 40·5. $C_{15}BrF_{15}Sn$ requires C, 30·9; H, 0·0; Br, 11·4; F, 40·8%), $\nu_{max.}$ 1650, 1620, 1600, 1555sh, 1520, 1485, 1460sh, 1440sh, 1380, 1370sh, 1330, 1320, 1310, 1285, 1250, 1200, 1180, 1170, 1145, 1090, 1085, 1065sh, 1035, 1025, 1010, 1005sh, 970, 906, 883, 860, 840, 810, 750, 723, 710 cm.$^{-1}$.

Pentafluorophenylstannonic Acid.—Pentafluorophenyltin trichloride, digested in water, yielded *pentafluorophenylstannonic acid* (Found: C, 22·0; H, 1·2; F, 28·5. $C_6HF_5O_2Sn$ requires C, 22·6; H, 0·3; F, 29·8%), $\nu_{max.}$ 3600, 3350, 1650, 1620sh, 1550sh, 1520, 1485sh, 1460, 1450sh, 1390sh, 1380, 1365sh, 1320, 1280, 1140, 1080, 1060, 1000, 965, 890, 790, 725 cm.$^{-1}$.

*Reaction of Di-*o*-tolylbispentafluorophenyltin with Hydrogen Chloride.*—The tin compound (1·4 g., 2·2 mmoles) was treated with hydrogen chloride (2·2 mmoles) in a sealed tube. After 12 hr. the tube was opened; toluene was identified in the products by its infrared spectrum, and the residual oil after pumping gave the same infrared spectrum as bispentafluorophenyltin dichloride.

X-*Ray Powder Photography.*—A Guinier-type powder focussing camera was used. Photographs were taken on Ilford Industrial G *X*-ray film, with *X*-rays produced from a copper target.

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