373. *Aromatic Polyfluoro-compounds. Part XXII.*[1] *Some Transmetallation Reactions of Bispentafluorophenylmercury*

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Bispentafluorophenylmercury reacts with sulphur, selenium, and tin at elevated temperatures to give bispentafluorophenyl sulphide, bispentafluorophenyl selenide, and tetrakispentafluorophenyltin. Attempted reactions, under the same conditions, with aluminium, bismuth, cadmium, chromium, iron, zinc, phosphorus, and titanium gave mainly unreacted starting materials.

In a previous Paper[2] we reported the displacement of fluorine from bispentafluorophenylmercury with nucleophiles; we now describe some reactions in which the mercury is replaced by other elements.

Hydrocarbon alkyl and aryl mercurials undergo transmetallation reactions with comparative ease.[3] Diphenylmercury reacts with metals, for example bismuth, antimony, aluminium, and cadmium,[4] at 200—300°, though difficultly separable mixtures were often obtained. Metalloids such as sulphur and selenium have also been used.[5] This ease of reaction is not observed with the bisperfluoroalkylmercurials since no transmetallation reactions occur under similar conditions.[6]

It was thus of interest to establish whether a similar difference existed between the aryl- and perfluoroaryl-mercurials.

A series of reactions has been carried out, under conditions similar to those used in the hydrocarbon field, between bispentafluorophenylmercury and various elements. Only with sulphur, tin, and selenium was transmetallation observed.

Bispentafluorophenylmercury and sulphur reacted smoothly when heated in a sealed tube at 250° for seven days, to give bispentafluorophenyl sulphide in 82% yield. This sulphide could not be prepared by reaction of hexafluorobenzene with potassium pentafluorothiophenate owing to its rapid reaction with more pentafluorothiophenate to give polymeric material[7] and so the transmetallation represents the first synthesis. Oxidation of the sulphide to the sulphone with peracetic acid was not possible, paralleling the lack of reaction of bis-(2,3,5,6-tetrafluorophenyl) sulphide.[7]

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[1] Part XXI, Brooke, Forbes, Richardson, Stacey, and Tatlow, preceding Paper.
[2] Burdon, Coe, Fulton, and Tatlow, *J.*, 1964, 2673.
[3] Coates, " Organo Metallic Compounds," Methuen and Co., London, 1956, p. 43 ff.
[4] Hilpert and Gruttner, *Ber.*, 1913, **46**, 1675.
[5] Whitmore, " Organic Compounds of Mercury," Chemical Catalogue Co., New York, 1921.
[6] Emelèus and Haszeldine, *J.*, 1949, 2953.
[7] Robson, Stacey, Stephens, and Tatlow, *J.*, 1960, 4754.

Reduction of the sulphide with lithium aluminium hydride gave the known bis-(2,3,5,6-tetrafluorophenyl) sulphide,[7] showing that the penta- and tetra-fluorophenylthio-groups direct nucleophilic attack by lithium aluminium hydride into the position *para* to themselves. In this they resemble most other groups of the type C_6F_5X. Bispentafluorophenyl sulphide was also obtained by reaction of pentafluorophenylmercuric chloride [8] with sulphur under conditions similar to those described.

In a similar manner bispentafluorophenyl selenide was prepared in 75% yield from bispentafluorophenylmercury and selenium powder.

The reaction of bispentafluorophenylmercury and metallic tin afforded a 60% yield of tetrakispentafluorophenyltin, made previously [9] from the reaction of pentafluorophenylmagnesium bromide and tin tetrachloride. Reaction of the tin compound with sulphur for two days at 280° gave a 98% recovery of starting material; under the same conditions tetraphenyltin gives diphenyl sulphide.[10]

Bispentafluorophenylmercury appeared to react with red phosphorus (metallic mercury was formed) when the mixture was heated for seven days at 250°. However, the organic product was an intractable gum, the infrared spectrum of which was unlike that of trispentafluorophenylphosphine [11] and showed only aromatic ring and C–F stretching frequencies. The organic product was shown to contain no mercury by reaction with hydrogen sulphide.[2]

Reaction of titanium and of zinc with the mercurial gave droplets of mercury, but no tractable products could be isolated. In the case of zinc the product $[(C_6F_5)_2Zn]$ is known to be relatively unstable [12] and the titanium derivative would also be expected to be unstable and hence difficult to isolate.

With the other metals tried, no reaction appeared to occur, the recovery of starting material being high in each case. Diphenylmercury reacts with many of these metals under similar conditions.[4]

Thus it seems that although bispentafluorophenylmercury is more reactive than are the perfluoroalkylmercurials towards other elements, it resembles the perfluoroalkylmercurials rather than the hydrocarbon mercurials in its behaviour.

EXPERIMENTAL

Bispentafluorophenyl Sulphide.—(*a*) *From bispentafluorophenylmercury.* Bispentafluorophenylmercury [8,13] (1·07 g., 0·002 mole) and flowers of sulphur (0·16 g., 0·002 mole) were heated in a sealed tube at 250° for 7 days. The resultant yellow-brown crystalline mass was extracted with warm ether (20 ml.). The residual sulphur and mercuric sulphide (0·41 g.) were filtered off. After evaporation of the ether *in vacuo* there remained yellow-brown crystals (0·66 g.), m. p. 62—70°. Sublimation *in vacuo* at 70° followed by crystallisation from ethanol afforded *bispentafluorophenyl sulphide* (0·6 g.), m. p. 84—85° (Found: C, 39·5; H, 0·0. $C_{12}F_{10}S$ requires C, 39·4; H, 0·0%).

(*b*) *From pentafluorophenylmercuric chloride.* The mercurial [8] (0·2 g., 0·0005 mole) and flowers of sulphur (0·016 g., 0·002 mole) were heated in a sealed tube at 250° or 6 days. Isolation as in (*a*) afforded bispentafluorophenyl sulphide (0·06 g.), identical with the specimen prepared as described in (*a*).

Bis-(2,3,5,6-*tetrafluorophenyl*) *Sulphide.*—Bispentafluorophenyl sulphide (0·54 g.) was refluxed with a solution of lithium aluminium hydride (0·23 g.) in dry ether (15 ml.) for 24 hr. After the mixture had been cooled, 5N-sulphuric acid was added dropwise to destroy excess of lithium aluminium hydride. The ether layer was removed and the aqueous layer was extracted (2 × 5 ml.) with ether. The combined ether layers were dried ($MgSO_4$) and the ether evaporated to leave bis-(2,3,5,6-tetrafluorophenyl) sulphide (0·3 g.), m. p. 41° (lit.,[7] 44°), identified by infrared spectroscopy.

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[8] Chambers, Coates, Livingstone, and Musgrave, *J.*, 1962, 4367.

[9] Holmes, Peacock, and Tatlow, *Proc. Chem. Soc.*, 1963, 108.

[10] Bost and Borgstrom, *J. Amer. Chem. Soc.*, 1929, **51**, 1924.

[11] Pummer, private communication.

[12] Noltes and Van den Huche, *J. Organometallic Chem.*, 1964, **1**, 377.

[13] Coe, Stephens, and Tatlow, *J.*, 1962, 3227.

Bispentafluorophenyl Selenide.—Bispentafluorophenylmercury (1·0 g.) and selenium powder (0·2 g.) were heated in a sealed tube at 240° for 7 days. The resulting black powder was extracted with refluxing ether (50 ml.) for 1 hr. The residue of mercury selenide and selenium was filtered off and the ethereal solution was evaporated to leave strong-smelling yellow crystals (0·6 g.) which were purified by repeated sublimation at 80°/12 mm. to give *bispentafluorophenyl selenide*, m. p. 73—74° (Found: C, 35·0; H, 0·2. $C_{12}F_{10}Se$ requires C, 34·9; H, 0·0%).

Tetrakispentafluorophenyltin.—The mercurial (0·5 g.) and powdered tin (0·5 g.) were heated in a sealed tube at 260° for 9 days. The black mass obtained was extracted with boiling acetone. Evaporation of the acetone afforded tetrakispentafluorophenyltin (0·21 g.), m. p. and mixed m. p. with an authentic specimen [9] 218—219° (lit.,[9] 218—219°).

Reaction of Bispentafluorophenylmercury with Other Elements.—Experiments similar to those described above were carried out with various other elements as detailed below.

Element	Time	Temp.	% Starting material recovered	Element	Time	Temp.	% Starting material recovered
B	9 days	260°	74	Cd	4 days	250°	90
Al	7 ,,	240	75	Ti	6	250	74 [a]
Fe	7 ,,	250	76	P	7 ,,	250	0 [a,b]
Cr	7 ,,	250	70	Zn	6 ,,	250	0 [a,b]

[a] Droplets of metallic mercury were formed. [b] An intractable gum was the only organic product.

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