

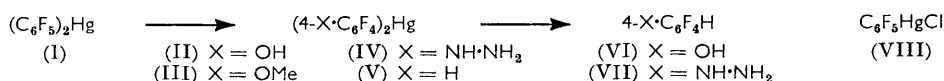
512. Aromatic Polyfluoro-compounds. Part XVII.¹ The Reaction of Bis(pentafluorophenyl)mercury with Nucleophiles.

By J. BURDON, P. L. COE, M. FULTON, and J. C. TATLOW.

Bis(pentafluorophenyl)mercury (I) reacts with potassium hydroxide, sodium methoxide, and hydrazine to give the corresponding 4,4'-disubstituted octafluorodiphenylmercurials (II—IV). With methyl-lithium, metal exchange occurs. Pentafluorophenylmercury chloride (VIII) gives bis-2,3,5,6-tetrafluoro-4-methoxyphenylmercury (III) and bis(pentafluorophenyl)mercury (I) with sodium methoxide and hydrazine, respectively.

EARLIER Papers² described nucleophilic replacements of fluorine in many aromatic polyfluoro-compounds. We have now extended this work to include bis(pentafluorophenyl)mercury (I)^{3,4} and pentafluorophenylmercury chloride (VIII).⁴

Bis(pentafluorophenyl)mercury (I) reacted quite straightforwardly with potassium hydroxide in *t*-butyl alcohol and with sodium methoxide in methanol to give the 4,4'-dihydroxy-(II) and 4,4'-dimethoxy-octafluorodiphenylmercurial (III), respectively, in good yield. These compounds were related by methylation of the dihydroxy-compound to the dimethoxide with diazomethane. Cleavage of the mercurial (II) with hydrogen sulphide gave⁵ the known 2,3,5,6-tetrafluorophenol (VI), thus proving that the oxygen functions of compounds (II) and (III) were in the 4,4'-positions. Although it is known⁶ that hydrogen sulphide will cleave diphenylmercury, the reaction has not been studied extensively. In fact, diphenylmercury and all the fluorinated mercurials described in this Paper reacted very rapidly with hydrogen sulphide, under our conditions, to give mercuric sulphide.



The reaction of hydrazine with bis(pentafluorophenyl)mercury (I) was more complex, since some mercury (41%) was formed. Three organic products were isolated, namely, bis-2,3,5,6-tetrafluoro-4-hydrazinophenylmercury (IV) (56%), pentafluorobenzene⁷ (9%), and 2,3,5,6-tetrafluorophenylhydrazine (VII)⁸ (29%). The last two products arise by extrusion of mercury, and the first is the expected di-replacement product; it was identified by conversion into the hydrazine (VII)⁸ by treatment with concentrated hydrochloric acid, a reagent known⁹ to cleave carbon-mercury bonds.

This extrusion of mercury by hydrazine was unexpected in that it did not occur with diphenylmercury, at least under the conditions used by us. The hydrazine (VII) could

¹ Part XVI, Letchford, Patrick, and Tatlow, *J.*, 1964, 1776.

² Tatlow, *Endeavour*, 1963, **22**, 89, and references cited therein.

³ Coe, Stephens, and Tatlow, *J.*, 1962, 3227.

⁴ Chambers, Coates, Livingstone, and Musgrave, *J.*, 1962, 4367.

⁵ Brooke, Forbes, Richardson, and Tatlow, (Part XX), forthcoming publication.

⁶ McCutchan and Kobe, *Ind. Eng. Chem.*, 1954, **46**, 675.

⁷ Stephens and Tatlow, *Chem. and Ind.*, 1957, 821.

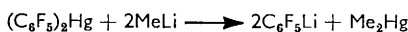
⁸ Brooke, Burdon, Stacey, and Tatlow, *J.*, 1960, 1768.

⁹ Dessy and Jin-Young Kim, *J. Amer. Chem. Soc.*, 1961, **83**, 1167.

arise by extrusion of mercury from the hydrazino-mercurial (IV), or by the hydrazination of the pentafluorobenzene from the initial extrusion, since this reaction gives the same product.⁸ The extrusions can be partly rationalised if they involve some type of nucleophilic attack by hydrazine on the mercury atom; the greater electronegativity of polyfluoroaryl groups, as compared to aryl, would make the polyfluorinated mercurials more susceptible to nucleophilic attack at the mercury than the non-fluorinated compounds. This cannot be the complete explanation since other nucleophiles (hydroxide and methoxide) did not cause any extrusion of mercury from bispentafluorophenylmercury. It is probably relevant that hydrazine, like chloride ion (in hydrochloric acid), can co-ordinate¹⁰ with mercury salts (*e.g.*, HgCl_4^{2-} , $\text{HgCl}_2 \cdot \text{N}_2\text{H}_4$); whereas reagents which do not cleave mercurials (*e.g.*, sulphuric acid, nitric acid, hydroxide ion) are not known¹⁰ to co-ordinate thus.

Lithium aluminium hydride reacted rapidly with bispentafluorophenylmercury (I), again with the extrusion of mercury and the formation of pentafluorobenzene.

With methyl-lithium it was apparent that metal exchange was taking place:



When this reaction was quenched with water after about five minutes at room temperature, similar amounts of pentafluorobenzene and dimethylmercury were obtained, together with a 40% recovery of bispentafluorophenylmercury (I). The direction of this metal exchange is as expected, the lithium compound of the more acidic hydrocarbon (pentafluorobenzene) being formed.

Pentafluorophenylmercury chloride (VIII)⁴ reacted with hydrazine under mild conditions to give bispentafluorophenylmercury (I) in good yield. Similar transformations of arylmercury halides into diarylmercurials can be effected with this and other reducing agents,¹¹ and also with alkali-metal alkoxides.¹² Also, sodium methoxide, under drastic conditions, converted the chloride (VIII) into the dimethoxy-compound (III), presumably by way of bispentafluorophenylmercury.

Bispentafluorophenylmercury and the presumed intermediates $\text{C}_6\text{F}_5 \cdot \text{Hg} \cdot \text{C}_6\text{F}_4\text{Y}$ are further examples² of $\text{C}_6\text{F}_5\text{X}$ compounds which undergo nucleophilic replacement of fluorine from the position *para* to X. In previous Papers,¹³ we argued that significant replacement other than *para* would only occur if X were powerfully electron-donating or possibly electron-attracting, with the reaction rates being much retarded or accelerated, respectively, as compared with pentafluorobenzene. Our present finding that bispentafluorophenylmercury reacts at the 4,4'-positions at a rate qualitatively not very different from that of pentafluorobenzene is consistent with this suggestion.

EXPERIMENTAL

Bis-2,3,5,6-tetrafluoro-4-hydroxyphenylmercury (II).—Bispentafluorophenylmercury (I)^{3,4} (2.0 g.), potassium hydroxide (1.0 g.), and *t*-butyl alcohol (2 ml.) were heated for 1 hr. at 100°. Water (120 ml.) and 5*N*-potassium hydroxide (10 ml.) were added to the solid mixture, and the solution was extracted with ether, acidified, and re-extracted with ether. Evaporation of the second extract gave the *mercurial* (II) (1.1 g.), m. p. >400° (slight decomp. at *ca.* 200°) (from benzene) (Found: C, 26.9; H, 0.7. $\text{C}_{12}\text{H}_2\text{F}_8\text{HgO}_2$ requires C, 27.2; H, 0.4%). This phenol gave a pink colour with methanolic ferric chloride.

Bis-2,3,5,6-tetrafluoro-4-methoxyphenylmercury (III).—(a) From bispentafluorophenylmercury (I). 0.5*N*-Sodium methoxide in methanol (50 ml.) and bispentafluorophenylmercury (3.0 g.)

¹⁰ J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Longmans, London, 1923, p. 848 *et seq.*

¹¹ Maynard, *J. Amer. Chem. Soc.*, 1924, **46**, 1510; Gilman and Barnett, *Rec. Trav. chim.*, 1936, **55**, 563.

¹² Whitmore, Hanson, and Carnahan, *J. Amer. Chem. Soc.*, 1929, **51**, 894; Beattie and Whitmore, *ibid.*, 1933, **55**, 1128.

¹³ Brooke, Burdon, and Tatlow, *J.*, 1962, 802; Alsop, Burdon, and Tatlow, *J.*, 1962, 1801.

were refluxed together for 24 hr. The yellow mixture was poured into water (50 ml.) and the crude mercurial (III) (2.5 g.), m. p. 145—150°, was precipitated. The pure compound had m. p. 153—154° (from ethanol) (Found: C, 30.1; H, 1.5. $C_{14}H_6F_8HgO_2$ requires C, 30.1; H, 1.1%).

(b) From bis-2,3,5,6-tetrafluoro-4-hydroxyphenylmercury (II). A 0.15M-solution of diazomethane in ether was added dropwise, with stirring, to a cooled (0°) suspension of the phenol (II) (0.25 g.) in ether (20 ml.) until the yellow colour of diazomethane persisted. Evaporation of the ether and recrystallisation of the residue from ethanol gave the dimethoxy-compound (III) (0.16 g.), identical (mixed m. p. and infrared spectrum) with the specimen obtained in (a).

Reaction of Bis-2,3,5,6-tetrafluoro-4-hydroxyphenylmercury (II) with Hydrogen Sulphide.—5N-Sulphuric acid was added dropwise, with stirring, to a mixture of sodium hydrogen sulphide (0.56 g.), the mercurial (II) (0.25 g.), and ether (20 ml.) until the evolution of hydrogen sulphide ceased. The ether phase was separated, dried ($MgSO_4$), and evaporated, to leave 2,3,5,6-tetrafluorophenol (VI) (0.1 g.) as a semi-solid residue (lit.,⁵ m. p. 30°), identified from its infrared spectrum.⁵

Reaction of Bis-pentafluorophenylmercury (I) with Hydrazine.—The mercurial (2.9 g.) was refluxed with hydrazine hydrate (2.9 g.) in ethanol (20 ml.) for 6 hr., by which time mercury droplets (ca. 0.45 g.) and a white solid had formed. The mercury was removed and the organic liquids were distilled from the remaining aqueous ethanolic suspension. Ether (10 ml.) was added to the distillate, and this was dried ($MgSO_4$) and separated by gas chromatography [16 ft. \times 1½ in. column; dinonyl phthalate-kieselguhr (1:2); temp. 100°; nitrogen carrier gas (20 l./hr.)], to give ether, ethanol, and pentafluorobenzene⁷ (0.16 g.), identified by infrared spectroscopy. The aqueous residue from the distillation was poured into a mixture of water (400 ml.) and ethanol (20 ml.), and set aside for 24 hr. with occasional stirring and breaking-up of lumps of solid. The solid was filtered off, dissolved in dimethylformamide, and precipitated by water, to give bis-2,3,5,6-tetrafluoro-4-hydrazinophenylmercury (IV) (1.70 g.), m. p. 225—228° (Found: C, 25.9; H, 1.6. $C_{12}H_6F_8HgN_4$ requires C, 25.8; H, 1.1%). This compound decomposed on exposure to air or light. It gave a bisbenzaldehyde derivative, m. p. 231—232° (from aqueous acetone) (Found: C, 42.5; H, 2.3. $C_{26}H_{14}F_8HgN_4$ requires C, 42.5; H, 1.9%).

The aqueous filtrate (after removal of the precipitated bishydrazino-compound) was extracted with ether, to yield 2,3,5,6-tetrafluorophenylhydrazine (VII) (0.30 g.), m. p. 82—85° (lit.,⁸ 90—91.5°), identified by mixed m. p. (87—89°) and infrared spectroscopy.

Reaction between Bis-2,3,5,6-tetrafluoro-4-hydrazinophenylmercury (IV) and Hydrochloric Acid.—The mercurial (0.2 g.) was refluxed with 11N-hydrochloric acid (10 ml.) until it dissolved (25 min.). The solution was made alkaline and the 2,3,5,6-tetrafluorophenylhydrazine (VII) was isolated by ether extraction (0.08 g.), m. p. 85—87°, identified by mixed m. p.⁸ and infrared spectroscopy.

Bis-2,3,5,6-tetrafluorophenylmercury (V).—Bis-2,3,5,6-tetrafluoro-4-hydrazinophenylmercury (IV) (4.71 g.) was refluxed for 30 min. with Fehling's solution (300 ml.). The mixture was allowed to cool and the brown solid was filtered off, dried, sublimed at 100° *in vacuo*, and crystallised from ether, to yield the mercurial (V) (1.1 g.), m. p. 125° (softens at ca. 100° with sublimation) (Found: C, 28.9; H, 0.6. $C_{12}H_2F_8Hg$ requires C, 28.9; H, 0.4%).

Reaction between Bis-pentafluorophenylmercury (I) and Methyl-lithium.—1.16N-Methyl-lithium in ether (21.5 ml.), at 0°, was added during 2 min., with stirring, to a cooled (0°) solution of bis-pentafluorophenylmercury (I) (5.0 g.) in ether (50 ml.). The solution became deep yellow changing to pale green after about 5 min. Water (30 ml.) was added and the ether layer was separated, washed with water, and dried ($MgSO_4$). Analytical gas chromatography (on dinonyl phthalate-kieselguhr) showed, besides ether, two peaks of similar areas with retention times corresponding to pentafluorobenzene and dimethylmercury. The ether solution was distilled through a 10-cm. Vigreux column, to give three fractions which were identified by infrared spectroscopy as ether, mainly pentafluorobenzene (0.65 g.), and a mixture of pentafluorobenzene and dimethylmercury. This third fraction was converted, by refluxing with ethanol (5 ml.) and mercuric chloride (0.5 g.), into methylmercury chloride (1.05 g.), m. p. 171—172° (lit.,¹⁴ 170°). The residue (2.0 g.) from the ether distillation was identified as bis-pentafluorophenylmercury by m. p., mixed m. p., and infrared spectroscopy.

Reaction of Pentafluorophenylmercury Chloride (VIII).—(a) *With hydrazine.* Hydrazine hydrate (0.5 g.) was added dropwise to pentafluorophenylmercury chloride⁴ (VIII) (0.2 g.) in

¹⁴ Seidel, *J. prakt. Chem.*, 1884, **29**, 134.

ethanol (20 ml.). An immediate reaction occurred, and, after 5 min., a grey precipitate appeared. After 2 hr. at room temperature, the ethanol solution was decanted from the mercury mirror (ca. 0.05 g.) into water (50 ml.). The precipitate which formed was identified as bispentafluorophenylmercury (0.07 g.) by m. p., mixed m. p., and infrared spectroscopy.

(b) *With sodium methoxide.* The chloride (1.0 g.) was refluxed with 1.1N-sodium methoxide in methanol (18 ml.) for 22 hr. The mixture was poured into water (400 ml.), to give a precipitate of bis-2,3,5,6-tetrafluoro-4-methoxyphenylmercury (III) (0.6 g.), m. p. 147°, identified by mixed m. p. and infrared spectroscopy.

We thank the Imperial Smelting Corporation for a grant to M. F.

THE CHEMISTRY DEPARTMENT,

THE UNIVERSITY, EDGBASTON, BIRMINGHAM 15.

[Received, November 14th, 1963.]
