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ORGANOMERCURY COMPOUNDS

XVII*. THE MERCURATION OF 1,2,3,4-TETRAFLUOROBENZENE, 1,2,3,5-TETRAFLUOROBENZENE, 2,3,5,6-TETRAFLUOROANISOLE, AND 2,3,4,5-TETRAFLUORONITROBENZENE

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SUMMARY

The tetrafluorophenylmercuric trifluoroacetates, $RHgO_2CCF_3$ (R = o-HC_6F_4, m-HC_6F_4, p-$MeOC_6F_4$, or o-$O_2NC_6F_4$), and the dimercurated tetrafluorobenzenes o-$(CF_3CO_2Hg)_2C_6F_4$ and m-$(CF_3CO_2Hg)_2C_6F_4$ have been prepared by mercuration of the appropriate tetrafluorobenzenes with mercuric trifluoroacetate. Reaction of 1,2,3,4-tetrafluorobenzene with mercuric acetate did not give pure monomercurated or dimercurated products, but o-$HC_6F_4HgO_2CCH_3$ and o-$(CH_3CO_2Hg)_2C_6F_4$ were obtained analytically pure by treatment of the appropriate trifluoroacetates with acetic acid. The diarylmercurials R_2Hg (R = o-HC_6F_4, m-HC_6F_4, p-$MeOC_6F_4$, or o-$O_2NC_6F_4$) were prepared by symmetrization of the tetrafluorophenylmercuric trifluoroacetates with iodide or bromide ions in methanol or aqueous methanol. A good yield of $(p$-$MeOC_6F_4)_2Hg$, and low yields of crude $(m$-$HC_6F_4)_2Hg$ and $(o$-$O_2NC_6F_4)_2Hg$ were obtained by mercuration of the corresponding tetrafluorobenzenes under basic conditions, but $(o$-$HC_6F_4)_2Hg$ could not be obtained by this method. The halogeno derivatives RHgX (R = o-HC_6F_4 or m-HC_6F_4), o-$(XHg)_2C_6F_4$, and m-$(XHg)_2C_6F_4$ (X = Cl or Br) have been synthesized from the appropriate trifluoroacetates and hydrogen halides and/or by redistribution reactions of suitable mercurials and mercuric halides.

INTRODUCTION

Pentafluorobenzene and 1,2,4,5-tetrafluorobenzene can be mercurated by mercuric carboxylates[2,3], but forcing conditions are needed, since polyfluoroarenes are deactivated towards electrophilic attack[4–6] and hence mercuration by mercuric salts[7]. In addition, the compounds are readily mercurated by tetrabromomercurate(II) ions under basic conditions[3,8] (unusual behaviour for arenes[8]). To test whether these reactions are general routes to polyfluoroarylmercurials, we have now studied mercuration of 1,2,3,4-tetrafluorobenzene, 1,2,3,5-tetrafluorobenzene, 2,3,5,6-tetrafluoroanisole, and 2,3,4,5-tetrafluoronitrobenzene.

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* For Part XVI, see ref. 1.

RESULTS AND DISCUSSION

(*a*). *Mercuration with mercuric trifluoroacetate*

Reaction of mercuric trifluoroacetate with an excess of 1,2,3,4-tetrafluorobenzene or 1,2,3,5-tetrafluorobenzene and with equimolar amounts of 2,3,5,6-tetrafluoroanisole or 2,3,4,5-tetrafluoronitrobenzene at elevated temperatures (ca. 160°–200°) gave the corresponding tetrafluorophenylmercuric trifluoroacetates [reaction (1); R = o-HC_6F_4, m-HC_6F_4, p-$MeOC_6F_4$, or o-$O_2NC_6F_4$]*.

$$RH+Hg(O_2CCF_3)_2 \rightarrow RHgO_2CCF_3+CF_3CO_2H \qquad (1)$$

Refluxing 1,2,3,5-tetrafluorobenzene was also mercurated by mercuric trifluoroacetate. More severe conditions were needed for the mercuration of 2,3,4,5-tetrafluoronitrobenzene than for 2,3,5,6-tetrafluoroanisole (see Experimental), consistent with a mechanism involving electrophilic substitution. Reaction of mercuric trifluoroacetate with 1,2,3,4-tetrafluorobenzene or 1,2,3,5-tetrafluorobenzene (mole ratio 2/1) gave the corresponding bis(trifluoroacetatomercuri)tetrafluorobenzenes.

$$o\text{- or } m\text{-}H_2C_6F_4+2\,Hg(O_2CCF_3)_2 \rightarrow o\text{- or } m\text{-}(CF_3CO_2Hg)_2C_6F_4+2\,CF_3CO_2H \qquad (2)$$

Identities of the mercuration products were confirmed by ^{19}F NMR spectra (Experimental Section), their interpretation being aided by the observation that fluorines *ortho* to mercury resonate at lower fields than *meta* or *para* fluorines[9]. The aromatic fluorine resonances of o-$HC_6F_4HgO_2CCF_3$, m-$HC_6F_4HgO_2CCF_3$, p-$MeOC_6F_4HgO_2CCF_3$, and o-$(CF_3CO_2Hg)_2C_6F_4$ were similar to those of o-HC_6F_4HgCl[9], $(m\text{-}HC_6F_4)_2Hg$[9], p-$MeOC_6F_4Fe(CO)_2(\pi\text{-}C_5H_5)$[10], and octafluoroselanthrene[9] respectively. Comparison of the infrared spectra of the organomercuric trifluoroacetates with those of the corresponding chlorides, bromides, or diarylmercurials (Experimental Section) enabled $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ to be assigned to bands in the ranges 1690–1660 and 1430–1400 cm^{-1} respectively, the values being similar to those for other polyfluoroarylmercuric trifluoroacetates[2,3].

(*b*). *Mercuration with mercuric acetate*

Impure o-$HC_6F_4HgO_2CCH_3$ and o-$(CH_3CO_2Hg)_2C_6F_4$ were obtained from heating mercuric acetate with 1,2,3,4-tetrafluorobenzene in suitable stoichiometric ratios at 160°. The compounds were identified by infrared spectroscopy, the analytically pure compounds being prepared by metathesis reactions:

$$o\text{-}HC_6F_4HgO_2CCF_3+CH_3CO_2H \rightarrow o\text{-}HC_6F_4HgO_2CCH_3+CF_3CO_2H$$

$$o\text{-}(CF_3CO_2Hg)_2C_6F_4+2\,CH_3CO_2H \rightarrow o\text{-}(CH_3CO_2Hg)_2C_6F_4+2\,CF_3CO_2H$$

Intense infrared absorption of the acetatomercuri- compounds near 1600 and 1300 cm^{-1} may be assigned to carbon–oxygen stretching.

(*c*). *(Halogenomercuri)tetrafluorobenzenes*

Several (chloromercuri)- and (bromomercuri)tetrafluorobenzenes have been prepared by metathesis reactions of the (trifluoroacetatomercuri)tetrafluorobenzenes

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* For convenience, positions of substituents other than fluorine are indicated in formulae.

with hydrogen halides, and by rearrangement reactions of the appropriate bis(tetrafluorophenyl)mercurials [preparations—sections (*d*) and (*e*)] with mercuric halides.

$$\mathrm{RHgO_2CCF_3 + HX \rightarrow RHgX + CF_3CO_2H}$$

$$\mathrm{R = \mathit{o}\text{-}HC_6F_4, X = Cl; R = \mathit{m}\text{-}HC_6F_4, X = Cl\ or\ Br}$$

$$\mathit{o}\text{- or } \mathit{m}\text{-}\mathrm{(CF_3CO_2Hg)_2C_6F_4 + 2\,HX \rightarrow \mathit{o}\text{- or } \mathit{m}\text{-}(XHg)_2C_6F_4 + 2CF_3CO_2H} \qquad (3)$$

$$\mathrm{X = Cl\ or\ Br}$$

$$\mathrm{R_2Hg + HgX_2 \rightarrow 2\,RHgX} \qquad (4)$$

$$\mathrm{R = \mathit{o}\text{-}HC_6F_4\ or\ \mathit{m}\text{-}HC_6F_4; X = Cl\ or\ Br}$$

2,3,4,5-Tetrafluorophenylmercuric chloride has previously been prepared by reaction (4)[9] under slightly different conditions from those used in the present study. 1,2-Bis(bromomercuri)tetrafluorobenzene could only be obtained in crude form by (3), but was prepared pure by rearrangement of perfluorotribenzo[*b,e,h*][1,4,7]trimercuronin:

$$\mathrm{(-\mathit{o}\text{-}HgC_6F_4-)_3 + 3\,HgBr_2 \rightarrow 3\,\mathit{o}\text{-}(BrHg)_2C_6F_4}$$

(*d*). *Preparations of bis(tetrafluorophenyl)mercurials by symmetrization*

The tetrafluorophenylmercuric trifluoroacetates obtained by reaction (1) underwent extremely rapid symmetrization with iodide or bromide ions in methanol or aqueous methanol at room temperature to give the corresponding bis(tetrafluorophenyl)mercurials [reaction (5); $\mathrm{R = \mathit{o}\text{-}HC_6F_4}$, $\mathit{p}\text{-}\mathrm{MeOC_6F_4}$, or $\mathit{o}\text{-}\mathrm{O_2NC_6F_4}$, X = I; $\mathrm{R = \mathit{m}\text{-}HC_6F_4}$, X = Br].

$$\mathrm{2\,RHgO_2CCF_3 + 4\,X^- \rightarrow R_2Hg + HgX_4^{2-} + 2\,CF_3CO_2^-} \qquad (5)$$

The reaction proceeds far more readily than analogous rearrangements of (hydrocarbon)arylmercuric carboxylates[11]. This is important synthetically, since heating during the symmetrization of the fluoro-carbon compounds could lead to cleavage of the polyfluorophenyl–mercury bonds[12]. Other synthetic methods for the present bis(tetrafluorophenyl)mercurials are discussed in sections (*e*) and (*f*).

(*e*). *Preparations of bis(tetrafluorophenyl)mercurials by mercuration under basic conditions*

From reactions of the appropriate tetrafluorobenzenes with tetrabromomercurate(II) ions under alkaline conditions in aqueous t-butanol, a good yield of bis(4-methoxytetrafluorophenyl)mercury was obtained, but only low yields of crude bis(2,3,4,6-tetrafluorophenyl)mercury and bis(2-nitrotetrafluorophenyl)mercury [reaction (6); $\mathrm{R = \mathit{p}\text{-}MeOC_6F_4}$, $\mathit{m}\text{-}\mathrm{HC_6F_4}$, or $\mathit{o}\text{-}\mathrm{O_2NC_6F_4}$].

$$\mathrm{2\,RH + HgBr_4^{2-} + 2\,OH^- \rightarrow R_2Hg + 2\,H_2O + 4\,Br^-} \qquad (6)$$

All attempts to mercurate 1,2,3,4-tetrafluorobenzene under basic conditions failed (see Experimental). Yields of bis(polyfluorophenyl)mercurials obtained by (6) decrease in the sequence: $\mathrm{(C_6F_5)_2Hg}$[7] > $(\mathit{p}\text{-}\mathrm{MeOC_6F_4})_2\mathrm{Hg}$ > $(\mathit{p}\text{-}\mathrm{HC_6F_4})_2\mathrm{Hg}$[2] > $(\mathit{m}\text{-}\mathrm{HC_6F_4})_2\mathrm{Hg}$ > $(\mathit{o}\text{-}\mathrm{O_2NC_6F_4})_2\mathrm{Hg}$ > $(\mathit{o}\text{-}\mathrm{HC_6F_4})_2\mathrm{Hg}$. For $\mathrm{R_2Hg}$ ($\mathrm{R = C_6F_5}$, $\mathit{p}\text{-}\mathrm{HC_6F_4}$, $\mathit{m}\text{-}\mathrm{HC_6F_4}$, or $\mathit{o}\text{-}\mathrm{HC_6F_4}$), decreasing yields lie in the same order as decreasing acidities (in terms of rates of exchange with methoxide ions)[13] of the polyfluorobenzene reactants. Acidities of 2,3,5,6-tetrafluoroanisole and 2-nitrotetrafluorobenzene have not been determined, but it seems possible that the yield of $(p\text{-MeOC}_6F_4)_2Hg$ fits the pattern. The low yield of $(o\text{-O}_2NC_6F_4)_2Hg$ could indicate an unexpectedly low acidity for 2,3,4,5-tetrafluoronitrobenzene, possibly due to hydrogen-bonding with the nitro group. Alternatively, decomposition of the reactant or mercurial, *e.g.* by nucleophilic displacement of the nitro group, may occur during attempted mercuration. In pentafluorobenzene, exchange of the proton with base proceeds more rapidly than nucleophilic displacement of fluorine[13].

(*f*). *General remarks*

The present study, together with earlier results[2,3], establishes the mercuration reaction (1) as a general preparative method for polyfluoroarylmercurials, and, in conjunction with the facile symmetrization (5), as a general route to bis(polyfluoroaryl)mercurials, thus paralleling the importance of mercuration and symmetrization for (hydrocarbon) arylmercurials[11]. For R_2Hg ($R = o\text{-HC}_6F_4$, $m\text{-HC}_6F_4$, or $o\text{-O}_2NC_6F_4$), reactions (1) and (5) provide a preparation as convenient as, or more satisfactory than, other known syntheses, *viz.* the organolithium route[9] for $R = o\text{-HC}_6F_4$; the organolithium route[14], the reaction of $(m\text{-BrC}_6F_4)_2Hg$ with magnesium[14], symmetrization of $m\text{-HC}_6F_4HgO_3S\text{-}m\text{-HC}_6F_4$ obtained by sulphur trioxide elimination[1], and reaction (6) for $R = m\text{-HC}_6F_4$; the preparation and degradation of $(\text{-}o\text{-HgC}_6F_4\text{-})_3$ with nitric acid or nitrosyl chloride[15], and reaction (6) for $R = o\text{-O}_2NC_6F_4$. With a fairly wide range of polyfluoroarenes containing aryl–hydrogen bonds commercially available, reaction (1) could well become the most common route to polyfluoroaryl–mercury bonds. The thermal stabilities of mercuric trifluoroacetate and of the polyfluoroarylmercuric trifluoroacetates are clearly sufficient to withstand the forcing conditions often needed for mercuration.

By contrast, mercuration of polyfluoroarenes under basic conditions (6) is clearly *not* a general preparation of bis(polyfluoroaryl)mercurials [section (*e*)]. However, it should be the preferred synthesis for the limited number of compounds [currently $(C_6F_5)_2Hg$[7], $(p\text{-HC}_6F_4)_2Hg$[2], and $(p\text{-MeOC}_6F_4)_2Hg$] that can be obtained in good yield, since it is the simplest method available. The alternatives for bis(4-methoxytetrafluorophenyl)mercury are reactions (1) and (5), or the synthesis of bis(pentafluorophenyl)mercury and its reaction with methoxide ions[16].

EXPERIMENTAL

Microanalyses were by the Australian Microanalytical Service, Melbourne. Infrared spectra were obtained as described previously[3]. ^{19}F NMR and ^1H NMR spectra were obtained with a Varian A56/60 spectrometer. The fluorine resonances were measured from internal trichlorofluoromethane or hexafluorobenzene and the proton resonances from internal tetramethylsilane or acetone, but all values are quoted in ppm upfield from CCl_3F or downfield from Me_4Si using 163.7 ppm for the resonance of hexafluorobenzene[9] and 2.17 ppm for acetone[17].

Reagents

Polyfluoroaromatic compounds were obtained from Imperial Smelting, Bristol Organics, or Peninsular Chemresearch Inc.. Perfluorotribenzo[*b*,*e*,*h*] [1,4,7]-

trimercuronin was prepared by decarboxylation of mercuric tetrafluorophthalate[18], the infrared spectrum being in agreement with that reported[18], except for the slight modifications recently reported[1]. Sources of other reagents have been given[3].

Mercuration reactions at elevated temperatures

General. Reactions at elevated temperatures ($>100°$) were carried out in sealed evacuated Carius tubes. After reaction, trifluoroacetic or acetic acid and unreacted polyfluorobenzenes were removed under vacuum, leaving a residue of the (carboxylatomercuri)tetrafluorobenzene, which was purified as indicated below. Products were white solids unless indicated otherwise.

Mercuration with mercuric trifluoroacetate. 2,3,4,5-Tetrafluorophenylmercuric trifluoroacetate (nc) was obtained from reaction of mercuric trifluoroacetate (3.2 g, 7.5 mmole) and 1,2,3,4-tetrafluorobenzene (4.0 g, 27 mmole) at 160° (4 h), and was then sublimed at 110°/0.005 mm (yield 2.0 g, 58%), m.p. 89–90°. (Found: C, 20.4; H, 0.3; F, 29.1. $C_8HF_7HgO_2$ calcd.: C, 20.8; H, 0.2; F, 28.8%.) Infrared absorption: 1805 w (br), 1713 (sh), 1680 vs (br), 1650 (sh), 1625 m, 1600 (sh), 1574 w, 1553 w, 1520 vs (br), 1495 (sh), 1483 w, 1465 (sh), 1462 and 1458 vs, 1408 s, 1350 w, 1327 s, 1272 w, 1260 m, 1225 and 1195 vs (br), 1120 vs (br), 1083 vs, 1023 m, 1005 vs, 993 (sh), 901 w, 860 (sh), 853 s, 810 s, 783 s, 735 s, 705 s, 618 m, 553 m, 526 s and 392 m cm^{-1}. ^{19}F NMR spectrum ($CDCl_3$): 72.5 (s, 3 F, CF_3), 117.5 (m, 1 F, F 2), 136.2 (m, 1 F, F 5), and 152.1 (m, 2 F, F 3,4) ppm; (in acetone): 73.4 (CF_3), 117.5 (F 2), 139.6 (F 5) and 156.5 (F 3,4) ppm. PMR spectrum ($CDCl_3$): 7.50 (m, aromatic) ppm; (in acetone): 7.80 ppm.

2,3,4,6-Tetrafluorophenylmercuric trifluoroacetate (nc) was obtained from mercuric trifluoroacetate (8.0 g, 19 mmole) and 1,2,3,5-tetrafluorobenzene (4.4 g, 29 mmole) at 160° (1 h), and was purified by sublimation at 170°/0.005 mm (yield 2.0 g, 23%), m.p. 55–57°. (Found: C, 21.0; H, 0.4; F, 28.7%.) Infrared absorption: 3130 (sh), 3100 and 3084 w, 1785 (sh) (br), 1713 (sh), 1679 vs (br), 1630 s, 1613 (sh), 1590 m, 1570 w, 1501 vs, 1486 (sh), 1438 vs, 1419 m, 1400 vs, 1362 s, 1285 w (br), 1235 (sh), 1210, 1176 and 1147 vs (v br), 1059 vs, 1031 s (br), 860 and 856 m, 840 vs, 785 s, 738 vs, 723 (sh), 671 m, 610 w (br), 578 w, 565 w, 520 m (br) and 450 vw cm^{-1}. ^{19}F NMR spectrum (acetone): 73.3 (s, 3 F, CF_3), 92.5 (m, 1 F, F 6), 111.5 (m, 1 F, F 2), 131.0 (m, 1 F, F 4), and 165.2 (m, 1 F, F 3) ppm. The compound was handled in a nitrogen-filled glove bag to prevent moisture absorption, though rigorously anhydrous conditions were not needed. Continued sublimation after removal of the monomercurated product gave impure 1,3-bis(trifluoroacetatomercuri) in tetrafluorobenzene (2.6 g, 36%), m.p. 185–192° (infrared identification).

The required compound was also prepared by heating a solution of mercuric trifluoroacetate (8.0 g, 19 mmole) in 1,2,3,5-tetrafluorobenzene (8.0 g, 53 mmole) under reflux for 2 h. Removal of the volatiles under vacuum and sublimation of the residue gave the trifluoroacetate (6.0 g, 70%), m.p. 54–56°.

4-Methoxytetrafluorophenylmercuric trifluoroacetate (nc) was prepared from mercuric trifluoroacetate (1.2 g, 2.8 mmole) and 2,3,5,6-tetrafluoroanisole (0.53 g, 2.9 mmole) at 160° ($\frac{1}{4}$ h), and was then sublimed at 100°/0.001 mm (yield 1.0 g, 71%), m.p. 92–94°. (Found: C, 22.3; H, 0.6; F, 27.1. $C_9H_3F_7HgO_3$ calcd.: C, 21.9; H, 0.6; F, 27.0%.) Infrared absorption: 2964 w, 1711 (sh), 1676 vs (br), 1638 s, 1574 m, 1545 w, 1499 s, 1465 vs (br), 1438 m, 1414 s, 1384 s, 1335 (sh), 1282 (sh), 1266 m, 1205 vs (br), 1130 and 1115 vs (br), 1045 (sh), 966 vs (br), 948 s, 856 s, 804 m, 784 s, 734 s, 619 m, 569 w 523 m cm^{-1}. ^{19}F NMR spectrum (acetone): 73.1 (s, 3 F, CF_3), 119.2 (m, 2 F, F 2, 6) and 156.0 (m, 2F, F 4,5) ppm. The product was handled under nitrogen in a glove bag, although it was not strongly hygroscopic.

2-Nitrotetrafluorophenylmercuric trifluoroacetate (nc) was obtained from mercuric trifluoroacetate (8.0 g, 19 mmole) and 2,3,4,5-tetrafluoronitrobenzene (4.0 g, 21 mmole) at 180° (5 h) and 200° ($\frac{1}{2}$ h), and was recrystallized twice from benzene/hexane giving yellow plates (4.5 g, 47%), m.p. 152–154°. (Found: C, 19.3; F, 26.1; N, 3.0. $C_8F_7HgNO_4$ calcd.: C, 18.9; F, 26.2; N, 2.8%.) Infrared absorption: 1715 (sh), 1688 vs (br), 1654 m, 1628 vw, 1610 s, 1541 vs, 1499 vs, 1461 vs, 1418 (sh), 1409 s, 1345 (sh), 1338 vs, 1285 s, 1278 (sh), 1205 s, 1175 vs (v br), 1129 s, 1051 vs, 921 m, 851 m, 835 w, 819 m, 802 w, 780 s, 758 s, 735 s, 720 (sh), 610 w, 578 w, and 519 m cm^{-1}. ^{19}F NMR spectrum (benzene): 72.6 (s, 3 F, CF_3), 110.0 (m, 1 F, F 6), 136.0 (m, 1 F, F 3), 141.8 (m, 1 F, F 4 or 5) and 147.8 (m, 1 F, F 4 or 5) ppm. A separate reaction showed that the formation of the organomercuric trifluoroacetate was very incomplete after 1 h at 160°. Sublimation was unsatisfactory as a purification method, owing to decomposition.

1,2-Bis(trifluoroacetatomercuri)tetrafluorobenzene (nc). After reaction of mercuric trifluoroacetate (17.3 g, 41 mmole) and 1,2,3,4-tetrafluorobenzene (3.0 g, 20 mmole) at 160° (4 h) and removal of monomercurated tetrafluorobenzene by sublimation at 150°/0.005 mm, a residue of the required mercurial remained (14.0 g, 89%). (Found: C, 15.5; F, 24.1. $C_{10}F_{10}Hg_2O_4$ calcd.: C, 15.5; F, 24.5%.) Infrared absorption: 1795 w (br), 1660 vs (v br), 1635 (sh), 1620 w, 1595 and 1585 m, 1534 w, 1491 vs, 1430 and 1420 vs, 1363 m, 1321 m, 1302 m, 1264 w, 1258 (sh), 1195 vvs (br), 1145 vs (br), 1121 m, 1105 vs, 1038 m, 1016 vs, 935 w, 858 s, 828 s, 787 s, 777 m, 734 vs, 639 w, 611 m, 520 m and 420 w cm^{-1}. ^{19}F NMR spectrum (acetone): 73.5 (s, 6 F, CF_3), 115.6 (m, 2 F, F 3, 6) and 155.2 (m, 2 F, F 4, 5) ppm. Prolonged handling was carried out under nitrogen. The compound was also prepared by heating mercuric trifluoroacetate (8.0 g, 19 mmole) and 1,2,3,4-tetrafluorobenzene (5.6 g, 37 mmole) under reflux for 2 h. Isolation as above gave the dimercurated tetrafluorobenzene (3.7 g, 53%) and 2,3,4,5-tetrafluorophenylmercuric trifluoroacetate (1.0 g 12%) (infrared identifications).

1,3-Bis(trifluoroacetatomercuri)tetrafluorobenzene (nc). After reaction of mercuric trifluoroacetate (8.0 g, 19 mmole) and 1,2,3,5-tetrafluorobenzene (1.35 g, 9.0 mmole) in hexafluorobenzene (2 ml) at 160° (1 h) and removal of impure monomercurated benzene (1.1 g, 13%) at 130°/0.005 mm, the required compound was obtained (5.6 g, 77%), m.p. 193–195°, (Found: C, 15.5; F, 24.3%.) Infrared absorption: 1720 (sh), 1675 s (br), 1653 (sh), 1648 (sh), 1618 w, 1588 and 1575 w, 1460 vs (br), 1430 (sh), 1418 m, 1265 (sh), 1225 s, 1190 vs, 1132 s, 1063 (sh), 1055 m, 1049 (sh), 880 and 870 m, 857 m, 784 m, 733 m, 721 (sh), 620 w (br) and 523 w cm^{-1}. ^{19}F NMR spectrum (acetone, internal C_6F_6): 72.7 (m, F 2) and 73.4 (s, CF_3) (total integration 7 F), 110.9 (m, 2F, F 4, 6), and 163.3 (m, 1F, F 5) ppm upfield from $CFCl_3$.

Mercuration with mercuric acetate. 2,3,4,5-Tetrafluorophenylmercuric acetate (nc) was obtained impure from reaction of mercuric acetate (0.64 g, 2.0 mmole) and 1,2,3,4-tetrafluorobenzene (1.5 g, 10 mmole) at 160° (2$\frac{1}{2}$ h), and was sublimed at 140°/0.01 mm (yield 0.02 g, 2.5%), m.p. 178° (dec.), the infrared spectrum being similar to that of the authentic compound prepared by dissolution of 2,3,4,5-tetrafluorophenylmercuric trifluoroacetate (0.93 g, 2.0 mmole) in acetic acid (1 ml). After boiling the solution it was cooled and addition of a few drops of water caused deposition of the acetate, which was recrystallized from benzene (yield 0.51 g, 62%), m.p. 189–190°. (Found: C, 23.6; H, 1.0; F, 18.7. $C_8H_4F_4HgO_2$ calcd.: C, 23.5; H, 1.0; F, 18.6%.) Infrared absorption: 3080 w, 1688 w, 1630 (sh), 1610 vs (br), 1518 vs, 1510 (sh), 1500 (sh), 1465 and 1455 vs, 1440 (sh), 1428 m, 1395 m, 1375 vs, 1348 m, 1319 and 1300 vs (br), 1202 s, 1180 w, 1112 w, 1088 vs, 1044 w, 1022 s, 998 vs, 988 (sh), 933 m, 875 s, 812 s, 720 w, 699 vs, 648 w, 611 w, 552 m and 522 w (br) cm^{-1}. PMR spectrum [$(CD_3)_2SO$]: 7.31 (m, 1 H, aromatic) and 1.94 (s, 3 H, CH_3) ppm.

1,2-Bis(acetatomercuri)tetrafluorobenzene (nc) was obtained impure from reaction of mercuric acetate (5.2 g, 16 mmole) and 1,2,3,4-tetrafluorobenzene (1.2 g, 8.0 mmole) at 160° (4 h) (yield, ca. 4 g, 75%). The infrared spectrum was similar (but contained additional bands) to that of the authentic compound, prepared by suspending 1,2-bis(trifluoroacetatomercuri)tetrafluorobenzene (1.6 g, 2.1 mmole) in boiling glacial acetic acid (10 ml) for a few minutes. The required mercurial was filtered off and dried under vacuum at 40° (yield 1.3 g, 95%), m.p. >300°. (Found: C, 18.2; H, 0.9; F, 11.7. $C_{10}H_4F_6Hg_2O_4$ calcd.: C, 18.0; H, 0.9; F, 11.4%.) Infrared absorption: 1670 m, 1630 w, 1580 vs (v br), 1560 (sh), 1540 (sh), 1479 vs, 1427 vs, 1387 and 1372 s, 1320 vs (v br), 1252 w, 1220 m, 1194 m, 1168 m, 1121 w, 1097 vs, 1045 (sh), 1035 (sh), 1025 m, 1008 vs, 939 m, 825 s, 793 w, 777 m, 739 w, 692 vs, 640 m, 611 m and 511 m cm^{-1}. Although the compound was analytically pure, bands at 1670, 1220, 1198, and 1168 cm^{-1} could be due to the presence of residual trifluoroacetate. Insolubility in a wide range of solvents precluded recrystallization, or determination of the NMR spectrum. In a further preparation, mercuric acetate (0.32 g, 1.0 mmole) and 2,3,4,5-tetrafluorophenylmercuric trifluoroacetate (0.46 g, 1.0 mmole) were dissolved in acetic acid (5 ml) and the solvent was removed at the boiling point. The residue was further heated at 160° for 1 h. After washing the product with hot acetic acid, the required compound (0.55 g, 82%) was obtained (infrared identification).

(Halogenomercuri)tetrafluorobenzenes

2,3,4,5-*Tetrafluorophenylmercuric chloride. Method* (1). The compound was precipitated on dropwise addition of 35% hydrochloric acid (0.5 ml) to a solution of 2,3,4,5-tetrafluorophenylmercuric trifluoroacetate (0.50 g) in methanol (1 ml). The compound was washed with water, air-dried, then washed with hexane (yield 0.19 g, 45%), m.p. 152–153°, lit.[9] m.p. 150–152. (Found: C, 18.8; H, 0.2; Cl, 9.0; F, 19.6. C_6HClF_4Hg calcd.: C, 18.7; H, 0.3; Cl, 9.2; F, 19.7%.) Infrared absorption: 3060 vw, 1624 m, 1609 and 1599 (sh), 1525 vs (br), 1454 vs (br), 1348 w, 1326 m, 1277 m, 1203 m, 1098 (sh), 1088 s, 1024 w, 1000 vs, 990 (sh), 868 (sh), 861 s, 813 s, 709 s, 650 w, and 556 m cm^{-1}. The ^{19}F NMR spectrum in acetone was in agreement with that reported[9]. PMR spectrum (acetone, solvent and reference): 7.53 (m, aromatic) ppm.

Method (2). Bis(2,3,4,5-tetrafluorophenyl)mercury (0.42 g, 0.84 mmole) (preparation below) and mercuric chloride (0.25 g, 0.92 mmole) were heated for 2 min at 170°. Crystallization from benzene/hexane gave the required compound (0.40 g, 62%), m.p. 148–150° (IR identification).

2,3,4,5-*Tetrafluorophenylmercuric bromide* (nc) was prepared by heating equimolar amounts of bis(2,3,4,5-tetrafluorophenyl)mercury and mercuric bromide at 180° (10 min), followed by extraction with, and crystallization from hexane (yield, 13%) m.p. 150–151°. (Found: C, 16.7; H, 0.2; F, 17.6; Br, 18.8. C_6HBrF_4Hg calcd.: C, 16.8; H, 0.2; F, 17.7; Br, 18.6%.) Infrared absorption: 3075 vw, 1623 s, 1609 and 1598 m, 1550 w, 1515 vs (br), 1458 vs (br), 1349 m, 1325 s, 1277 s, 1200 s, 1092 vs, 1025 m, 1000 and 993 vs (br), 855 s, 810 s, 722 w, 709 s, 650 w, 556 s and 394 w cm^{-1}.

2,3,4,6-*Tetrafluorophenylmercuric chloride* (*nc*). *Method* (1). The compound was precipitated by addition of water (40 ml) to a mixture of the trifluoroacetate (0.50 g), 35% hydrochloric acid (1 ml) and methanol (2 ml), and was recrystallized from hexane (yield 0.10 g, 24%), m.p. 143–144°. (Found: C, 19.2; H, 0.4; F, 19.7%.) Infrared absorption: 3080 w, 1629 vs (br), 1591 m, 1510 (sh), 1485 vs (br), 1434 vs, 1423 (sh), 1365 s, 1290 w (br), 1228 s, 1143 s, 1060 vs, 1026 vs (br), 834 vs, 724 w, 674 m, 645 w, 585 m and 570 w cm^{-1}.

Method (2). Bis(2,3,4,6-tetrafluorophenyl)mercury (0.20 g, 0.40 mmole) and mercuric chloride (0.15 g, 0.55 mmole) at 170° ($\frac{1}{2}$ h) under vacuum, followed by crystallization from hexane gave the mercurial (0.22 g, 71%), m.p. 136–142°, mixed m.p. (with above product) 141–142°.

2,3,4,6-*Tetrafluorophenylmercuric bromide* (nc) was prepared and purified as in method (1) for the corresponding chloride (yield, 11%), m.p. 138–140°. (Found: C, 17.1; H, 0.2; F, 17.5%.) Infrared absorption: 3085 w, 1632 vs, 1623 m, 1592 s, 1510 (sh), 1495 vs (br), 1434 vs (br), 1423 (sh), 1364 s, 1294 m (br), 1285 (sh), 1240 (sh), 1228 s, 1147 and 1142 vs, 1066 vs, 1032 and 1022 vs, 836 vs, 722 w, 675 s, 642 w, 584 m, 569 m and 455 w cm^{-1}.

It was also obtained similarly to method (2), but with a reaction temperature of 180° (1 h) and sublimation at 170°/0.05 mm prior to recrystallization (yield 51%), m.p. 135–136°.

1,2-*Bis*(*chloromercuri*)*tetrafluorobenzene* (nc) was precipitated on addition of water to acidified (HCl) methanolic 1,2-bis(trifluoroacetatomercuri)tetrafluorobenzene (yield 63%), m.p. ca. 300° with dec. from 240°, (Found: C, 12.0; F, 12.2. $C_6Cl_2F_4Hg_2$ calcd.: C, 11.6; F, 12.3%.) Infrared absorption: 1620 s, 1608 (sh), 1580 s, 1518 w, 1485 vs, 1421 vs, 1356 m, 1318 s, 1297 s, 1254 m, 1120 m, 1090 vs, 1035 m, 1005 vs, 868 w (br), 825 vs, 773 vs, 720 w, 640 m and 472 w cm^{-1}. The mercurial was also precipitated in 92% yield on dropwise addition of concentrated hydrochloric acid to the trifluoroacetate in methanol, but redissolved in an excess of acid.

1,2-*Bis*(*bromomercuri*) *tetrafluorobenzene* (nc). Mercuric bromide (0.38 g, 1.1 mmole) and perfluorotribenzo[*b,e,h*][1,4,7]trimercuronin (0.35 g, 0.33 mmole) were refluxed together in methanol (10 ml) for 2 h. After cooling and filtration, the required compound was precipitated by addition of water and was air-dried (0.35 g, 49%), m.p. >300°. (Found: C, 10.9; Br, 22.4; F, 10.6. $C_6Br_2F_4Hg_2$ calcd.: C, 10.2; Br, 22.5; F, 10.7%.) Infrared absorption: 1619 s, 1590 s, 1512 (sh), 1484 vs, 1421 vs, 1352 m, 1315 s, 1292 s, 1260 w, 1118 w, 1092 vs, 1034 w, 1011 vs, 823 vs, 770 vs and 640 w cm^{-1}. When prepared by addition of concentrated hydrobromic acid to methanolic 1,2-bis(trifluoroacetatomercuri)tetrafluorobenzene, the compound was precipitated impure (Found: C, 11.8; Br, 19.4; F, 10.8 %), and attempted purification failed.

1,3-*Bis*(*chloromercuri*)*tetrafluorobenzene* (nc) was prepared as for the 1,2-bis(chloromercuri) analogue (yield, 90%), m.p. 220–222°. (Found: C, 11.4; Cl, 11.1; F, 11.9. $C_6Cl_2F_4Hg_2$ calcd.: C, 11.6; Cl, 11.4; F, 12.3%.) Infrared absorption: 1618 m, 1584 m, 1467 vs, 1432 m, 1370 w, 1335 w, 1230 w (br), 1073 s, 1050 m, 1035 (sh), 880 s, 721 m, 648 w and 580 vw cm^{-1}.

1,3-Bis(bromomercuri)tetrafluorobenzene (nc) was prepared as for *o*-$(ClHg)_2$-C_6F_4 (yield 99%) m.p. 200°. (Found: C, 10.7; F, 10.9%.) Infrared absorption: 1619 m, 1586 m, 1457 vs, 1435 m, 1372 w, 1334 w, 1220 w, 1064 s, 1050 (sh), 872 m, 721 w, 648 m and 432 w cm^{-1}.

Syntheses of bis(polyfluorophenyl)mercurials by symmetrization

The tetrafluorophenylmercuric trifluoroacetates, $RHgO_2CCF_3$, were treated with approximately twice the stoichiometric amount [eqn. (5)] of sodium or potassium iodide (R = *o*-HC_6F_4, *p*-$MeOC_6F_4$, or *o*-$O_2NC_6F_4$) or lithium bromide hydrate (R = *m*-HC_6F_4) in aqueous methanol (R = *o*-HC_6F_4) or methanol (R = *o*-HC_6F_4, *m*-HC_6F_4, *p*-$MeOC_6F_4$, or *o*-$O_2NC_6F_4$). The required mercurials were precipitated on addition of a large volume of water and were washed with water.

Bis(2,3,4,5-tetrafluorophenyl)mercury, prepared in aqueous methanol, was recrystallized from petroleum ether (b.p. 90–100°) (yield, 48%), m.p. 130–131°, lit.[9,19] m.p. 127–129°; 134–136°. (Found: C, 29.4; H, 0.6; F, 30.6. $C_{12}H_2F_8Hg$ calcd.: C, 28.9; H, 0.4; F, 30.5%.) Prepared in methanol, the compound was precipitated pure (yield 55%), m.p. 130–131°. (Found: C, 28.9; H, 0.4; F, 30.7%.) Infrared absorption: 3070 w, 1735 w, 1624 s, 1619 (sh), 1608 m, 1599 m, 1552 m, 1519 vs, 1499 (sh), 1446 vs (br), 1351 and 1346 m, 1315 vs, 1293 w, 1281 m, 1276 (sh), 1253 m, 1207 m, 1200 vs, 1183 m, 1123 w, 1112 w, 1082 vs, 1021 m, 1001 vs, 990 (sh), 872 vs, 813 vs, 721 m, 705 vs, 653 w, 635 w, 560 m, 510 w and 404 m cm^{-1}. The ^{19}F NMR spectrum in acetone was in agreement with that reported[9].

Bis(2,3,4,6-tetrafluorophenyl)mercury (yield, 78% from hexane), m.p. 84–84.5°, lit.[1] m.p., 84–85°. (Found: C, 29.1; H, 0.4; F, 30.7%.) Infrared absorption: 3090 w, 1628 vs, 1608 (sh), 1590 s, 1510 (sh), 1497 vs, ca. 1483 (sh), 1432 s, 1425 (sh), 1342 s, 1292 w, 1224 s (br), 1143 s, 1058 vs, 1030 vs (br), 839 vs, 720 w, 673 w, 587 m, 570 w and 453 w cm^{-1}. The ^{19}F NMR spectrum was in agreement with that reported[9].

Bis(4-methoxytetrafluorophenyl)mercury (yield 88% from benzene), m.p. 151–153°, lit.[16] 153–154°. The infrared spectrum was identical with that of the analytically pure compound, prepared by mercuration under basic conditions (below).

Bis(2-nitrotetrafluorophenyl)mercury (nc) was obtained as pale-yellow needles (76% from benzene), m.p. 199–200°. (Found: C, 24.8; F, 26.0; N, 4.6. $C_{12}F_8HgN_2O_4$ calcd.: C, 24.5; F, 25.8; N, 4.8%.) Infrared absorption: 1610 s, 1538 (sh), 1534 vs, 1494 vs, 1449 vs, 1363 (sh), 1335 vs, 1319 m, 1290 s, 1270 (sh), 1121 (sh), 1111 s, 1048 vs, 919 m, 816 m, 778 s, 762 s, 754 m, 720 w, 587 m, 533 w and 474 w cm^{-1}. ^{19}F NMR spectrum (acetone): 112.7 (m, F 6), 139.8 (m, F 3), 144.6 (m, F 4 or 5) and 151.3 (m, F 4 or 5) ppm. Integration of a similar spectrum for the compound in dioxane showed that equal numbers of the four different fluorine atoms were present. When prepared by degradation of perfluorotribenzo[*b*,*e*,*h*][1,4,7]trimercuronin, the compound has the same infrared spectrum[15].

Syntheses of bis(polyfluorophenyl)mercurials by mercuration under basic conditions

The reactants (Table 1) were stirred and heated under reflux in tert-butanol or aqueous tert-butanol, and the resulting solution was filtered into a large volume of water, precipitating any bis(polyfluorophenyl)mercurial formed. Purification and identification are given in Table 1.

TABLE 1

THE MERCURATION OF TETRAFLUOROBENZENES UNDER BASIC CONDITIONS

Reactants[a]					*Time* (*h*)	*Product* R_2Hg	
RH		$HgCl_2$	*NaOH*	$LiBr \cdot xH_2O$[b]		*Yield* (%)	*M.p.* (°C)
R	(*mmole*)	(*mmole*)	(*mmole*)	(*mmole*)			
$p\text{-MeOC}_6\text{F}_4$	3.9	2.0	12.5	24	4.0	54[c]	153.5–154
$m\text{-HC}_6\text{F}_4$	4.7	2.0	12.5	34	12.0	20[d]	74–76
$o\text{-O}_2\text{NC}_6\text{F}_4$	5.6	2.0	5.5	24	4.0	< 3[e]	
$o\text{-O}_2\text{NC}_6\text{F}_4$	8.2	2.0	9.0	24	6.0	< 1[f]	200–202
$o\text{-HC}_6\text{F}_4$	4.7	2.0	4.5	24	4.0		
$o\text{-HC}_6\text{F}_4$	4.6	2.0	12.5	36	13.0		
$o\text{-HC}_6\text{F}_4$	4.0	2.0	17.5	33	11.0		
$o\text{-HC}_6\text{F}_4$	5.6	2.0	17.5	34	4.5		
$o\text{-HC}_6\text{F}_4$[h]	6.7	2.0	36.0	70	2.0		
$o\text{-HC}_6\text{F}_4$[i]	6.7	2.0	22.0[g]	30	4.0		

[a] Solvent: t-$BuOH/H_2O$ 3/2, v/v, unless stated otherwise. Solvent volume 20 ml. [b] Contains ca. 15% water by weight, except for the last experiment where anhydrous LiBr was used (dried at 150°/0.05 mm). [c] After recrystallization from hexane (Found: C, 30.4; H, 1.4; F, 27.3. $C_{14}H_6F_8HgO_2$ calcd.: C, 30.1; H, 1.1; F, 27.2%). Infrared absorption: 2967 w, 1635 m, 1487 (sh), 1467 vs (vbr), 1438 m, 1401 (sh), 1373 s, 1190 m, 1091 vs, 969 vs, 803 m, 648 w, 572 m, 486 w, and 418 w cm^{-1}. ^{19}F NMR spectrum (acetone): 120.8 (m, 4 F, F 2, 2', 6, 6') and 156.0 (m, 4F, F 3, 3', 5, 5') ppm. [d] After sublimation under vacuum; infrared identification. [e] Infrared and ^{19}F NMR identification. [f] After recrystallization from benzene. [g] Sodium tert-butoxide. [h] Solvent: t-$BuOH/H_2O$ 1/1. [i] Solvent: t-BuOH dried over and distilled from $CaSO_4$.

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