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ORGANOMERCURY COMPOUNDS

XXIV* FACILE SYNTHESES OF POLYFLUOROARYLMERCURIALS BY MERCURATION REACTIONS

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Summary

The polyfluoroarylmercuric chlorides, RHgCl (R = C_6F_5, p-$MeOC_6F_4$, p-MeC_6F_4, m-HC_6F_4, o-HC_6F_4, p-HC_6F_4, m-$O_2NC_6F_4$, o-$O_2NC_6F_4$, p-BrC_6F_4, m-BrC_6F_4, o-BrC_6F_4, p-HOC_6F_4, p-$H_2NC_6F_4$, m-$HO_2CC_6F_4$, p-(p-HC_6F_4)C_6F_4, 3,5-$H_2C_6F_3$, 3-bromo-2,4,6-trifluorophenyl or 3-bromo-2,5,6-trifluorophenyl), and the bis(polyfluorophenyl)mercurials, R_2Hg (R = C_6F_5, p-$MeOC_6F_4$, p-MeC_6F_4, p-HC_6F_4, m-$O_2NC_6F_4$, o-$O_2NC_6F_4$, p-BrC_6F_4, m-BrC_6F_4, o-BrC_6F_4, p-HOC_6F_4, or p-$H_2NC_6F_4$) have been prepared by mercuration of the appropriate polyfluoroarenes with mercuric trifluoroacetate and trifluoromethanesulphonic acid in trifluoroacetic acid, followed by treatment of the products with hydrochloric acid (RHgCl derivatives) or potassium bromide (R_2Hg derivatives). For R = p-$MeOC_6F_4$, the actual mercuration product has been isolated and identified as 2,3,5,6-tetrafluoro-4-methoxyphenylmercuric trifluoromethanesulphonate. Interaction of mercuric trifluoroacetate with trifluoromethanesulphonic acid in trifluoroacetic acid yields mercuric trifluoromethanesulphonate, which is considered to be the mercurating agent, and which has been characterized as the complex, $[Hg(bpy)_3](O_3SCF_3)_2.H_2O$ (bpy = 2,2'-bipyridyl). The mercuration syntheses are very simple and convenient, and should become the preferred method for most polyfluoroarylmercurials.

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[*] Part XXIII, see Ref. [1].

Introduction

Polyfluoroaromatic compounds are deactivated to electrophilic attack [2, 3], and hence to mercuration [4]. Thus, forcing conditions (elevated temperatures/sealed tubes [5-7], or addition of the powerful Lewis acid, antimony pentafluoride [8]) are usually needed for the mercuration of polyfluoroarenes. Only 1,2,3,5-tetrafluorobenzene has been mercurated under comparatively mild conditions [6]. Some polyfluoroaromatic compounds can also be mercurated under alkaline conditions [6, 7, 9] (probably via polyfluorophenyl carbanion intermediates [9]) giving bis(polyfluorophenyl)-mercurials, but the method is restricted to the most acidic polyfluoroarenes. We have recently shown that the resistance of some polyfluoroaromatic compounds to thallation by thallic trifluoroacetate in trifluoroacetic acid can be overcome by addition of trifluoromethanesulphonic acid [10]. We now have examined the effect of the sulphonic acid on the mercuration of polyfluoroarenes.

Results and Discussion

(a) Mercuration of Polyfluoroarenes

The polyfluoroarenes (Table 1) were mercurated with mercuric trifluoroacetate in trifluoroacetic acid in the presence of trifluoromethanesulphonic acid.

$$\mathrm{RH} + \mathrm{Hg(O_2CCF_3)_2} + \mathrm{CF_3SO_3H} \longrightarrow \mathrm{RHgO_3SCF_3} + 2\,\mathrm{CF_3CO_2H} \quad (1)$$

The mercuration products were generally characterized as the corresponding organomercuric chlorides [Table 1; section (b)], which were formed by reaction (2).

$$\mathrm{RHgO_3SCF_3} + \mathrm{HCl} \longrightarrow \mathrm{RHgCl} + \mathrm{CF_3SO_3H} \quad (2)$$

However, the actual mercuration product was isolated in one case (R = p-MeOC_6F_4). It was identified as 2,3,5,6-tetrafluoro-4-methoxyphenylmercuric trifluoromethanesulphonate rather than the corresponding trifluoroacetate by analysis for sulphur, the observation of intense infrared absorption (1340, 1132, and 1015 cm^{-1}), attributable [11-13] to sulphur-oxygen stretching [$\nu(SO_2)$, A'; $\nu(SO_2)$, A''; and $\nu(SO)$, A'; respectively] of a coordinated sulphonate group, and by the absence of intense absorption at 1750-1600 cm^{-1}, characteristic [6, 7, 9] of $\nu_{as}(CO_2)$ of coordinated trifluoroacetate. Although the sulphur-oxygen stretching frequencies are similar to those of trimethyltin trifluoromethanesulphonate [13], which has a polymeric structure with bridging trifluoromethanesulphonate ligands, this does not necessarily establish similar sulphonate coordination in 2,3,5,6-tetrafluoro-4-methoxyphenylmercuric trifluoromethanesulphonate, since unidentate, bidentate, and bridging bidentate sulphonate groups have similar symmetry. Moreover, there is no marked difference between the sulphur-oxygen stretching frequencies of trimethyltin methanesulphonate (bridging bidentate sulphonate groups [13]) and methylmercuric methanesulphonate (unidentate sulphonate groups [11]). In view of the preference of mercury for linear two coordination in organomercurials [14], unidentate sulphonate coordination is most likely in *p*-$MeOC_6F_4HgO_3SCF_3$. Treatment of the compound with hydrochloric acid gave the corresponding chloride [reaction (2); R = *p*-$MeOC_6F_4$], hence it was not an equimolar mixture of bis(2,3,5,6-tetrafluoro-4-methoxyphenyl)mercury (unaffected by HCl) and mercuric trifluoromethanesulphonate (which would give $HgCl_3^-$ and/or $HgCl_4^{2-}$ with HCl). However, symmetrization into these compounds [reaction (3); R = *p*-$MeOC_6F_4$],

$$2\,RHgO_3SCF_3 \longrightarrow R_2Hg + Hg(O_3SCF_3)_2 \tag{3}$$

was evident soon after dissolution in acetone and was complete in 10 min. (see Experimental Section), and was also observed on washing the compound with water.

The reactivity order for mercuration of the polyfluorobenzenes, deduced from the preparative data (Table 1), generally conforms to that expected for electrophilic aromatic substitution, e.g. *p*-$MeOC_6F_4H$ > *p*-MeC_6F_4H > *p*-$H_2C_6F_4 \simeq C_6F_5H$ > *o*-$O_2NC_6F_4H$. A complete comparison could not be made between all the results, since comparable limiting conditions for substantial mercuration were not always established. Replacement of a fluorine by hydrogen *meta* to the point of attack markedly increases the ease of mercuration as indicated by the sequence, 1,3,5-$F_3C_6H_3$ > *m*-$H_2C_6F_4$ > C_6F_5H. Deactivation by *meta* fluorines has been observed in reactions of polyfluorobenzenes with other electrophilic reagents [2]. The very high reactivity of 2,3,5,6-tetrafluoroaniline shows that the electron-donating resonance effect of the amino group is operative despite the use of a strongly acidic medium. Presumably the electron withdrawing effect of the fluorine substituents causes substantial delocalisation of the nitrogen lone pair, resulting in low basicity (as observed for $C_6F_5NH_2$ [15]) but enhanced mercuration. Independent evidence for substantial π-donation by the amino group in *p*-$HC_6F_4NH_2$ has been provided by dipole moment measurements

(Continued on p.408)

TABLE 1

MERCURATION OF POLYFLUOROARENES WITH MERCURIC TRIFLUOROACETATE/TRIFLUOROMETHANESULPHONIC ACID [a]

Polyfluoroarene	Temp. (°C)	Time (h)	Product [b] RHgCl	Yield [c] (%)	Product [d] R_2Hg	Yield [c] (%)
C_6F_5H	73	1	C_6F_5HgCl	60	$(C_6F_5)_2Hg$	64
C_6F_5H [e]	73	1	C_6F_5HgCl	*ca*. 5 (crude)		
p-MeOC$_6$F$_4$H	25	0.17	*p*-MeOC$_6$F$_4$HgCl	72	(*p*-MeOC$_6$F$_4$)$_2$Hg	72
p-MeC$_6$F$_4$H	25	144	*p*-MeC$_6$F$_4$HgCl	60		
p-MeC$_6$F$_4$H	73	0.08	*p*-MeC$_6$F$_4$HgCl	78	(*p*-MeC$_6$F$_4$)$_2$Hg	76
m-H$_2$C$_6$F$_4$	25	12	*m*-HC$_6$F$_4$HgCl	64		
o-H$_2$C$_6$F$_4$	73	0.25	*o*-HC$_6$F$_4$HgCl	56		
p-H$_2$C$_6$F$_4$	73	1	*p*-HC$_6$F$_4$HgCl	63	(*p*-HC$_6$F$_4$)$_2$Hg	35
m-O$_2$NC$_6$F$_4$H	73	12	*m*-O$_2$NC$_6$F$_4$HgCl	50		
m-O$_2$NC$_6$F$_4$H	73	168			(*m*-O$_2$NC$_6$F$_4$)$_2$Hg	70 [f]
o-O$_2$NC$_6$F$_4$H	73	18	*o*-O$_2$NC$_6$F$_4$HgCl	14		
o-O$_2$NC$_6$F$_4$H	73	72			(*o*-O$_2$NC$_6$F$_4$)$_2$Hg	70
p-BrC$_6$F$_4$H	73	18	*p*-BrC$_6$F$_4$HgCl	80		
p-BrC$_6$F$_4$H	73	6			(*p*-BrC$_6$F$_4$)$_2$Hg	73
m-BrC$_6$F$_4$H	73	1.5	*m*-BrC$_6$F$_4$HgCl	73		

TABLE 1 (cont.)

Polyfluoroarene	Temp. (°C)	Time (h)	Product [b] RHgCl	Yield [c] (%)	Product [d] R_2Hg	Yield [c] (%)
m-BrC_6F_4H	73	4.5			(*m*-$BrC_6F_4)_2Hg$	64
o-BrC_6F_4H	73	24	*o*-BrC_6F_4HgCl	78		
o-BrC_6F_4H	73	5.5			(*o*-$BrC_6F_4)_2Hg$	52
p-HOC_6F_4H	25	0.03	*p*-HOC_6F_4HgCl	31 [g]	(*p*-$HOC_6F_4)_2Hg$	73
p-$H_2NC_6F_4H$	25	0.03	*p*-$H_2NC_6F_4HgCl$	69	(*p*-$H_2NC_6F_4)_2Hg$	71
m-$HO_2CC_6F_4H$	73	3	*m*-$HO_2CC_6F_4HgCl$	79		
(*p*-$HC_6F_4)_2$	73	18	*p*-(*p*-$HC_6F_4)C_6F_4HgCl$	41		
1,3,5-$H_3C_6F_3$	25	0.03	3,5-$H_2C_6F_3HgCl$	61		
$C_6H_2BrF_3$ [h]	73	0.5	C_6HBrF_3HgCl [h]	59		
$C_6H_2BrF_3$ [i]	73	3	C_6HBrF_3HgCl [i]	49		

[a] Mol. ratio 1:2. [b] After treatment of the product with HCl. [c] Yield of analytically pure product based on mercuric oxide. [d] After treatment of the product with NaBr. [e] In both CF_3CO_2H and $CF_3CO_2H:H_2O = 10:1$, v/v. No CF_3SO_3H added. [f] Yield based on *m*-$O_2NC_6F_4H$, as excess of mercurating agent used. [g] After two recrystallizations. One recrystallization gives 52% of slightly impure product. [h] 2-Bromo-1,3,5-trifluorobenzene giving 3-bromo-2,4,6-trifluorophenylmercuric chloride. [i] 1-Bromo-2,4,5-trifluorobenzene giving 3-bromo-2,5,6-trifluorophenylmercuric chloride.

[16]. A significant amount of dimercurated arene was formed on mercuration of 1,2,3,4-tetrafluorobenzene, but not 1,2,3,5-tetrafluorobenzene. Dimercuration of 1,2,4,5-tetrafluorobenzene was largely suppressed by use of a suitable excess of arene [see, however, section (c)].

The importance of trifluoromethanesulphonic acid in promoting mercuration can be seen from the results for pentafluorobenzene (Table 1). Under comparable conditions, substantial mercuration was achieved using mercuric trifluoroacetate and trifluoromethanesulphonic acid in trifluoroacetic acid, but negligible substitution occurred without the sulphonic acid. Reaction of mercuric trifluoroacetate in trifluoroacetic acid with trifluoromethanesulphonic acid resulted in precipitation of mercuric trifluoromethanesulphonate,

$$Hg(O_2CCF_3)_2 + 2CF_3SO_3H \longrightarrow Hg(O_3SCF_3)_2\downarrow + 2CF_3CO_2H \qquad (4)$$

which was identified by infrared spectroscopy (Experimental Section) and by conversion into the complex $[Hg(bpy)_3](O_3SCF_3)_2 \cdot H_2O$ (bpy = 2,2'-bipyridyl) (see below). For mercuration reactions, the precipitated mercuric sulphonate was dissolved by addition of water ($H_2O:CF_3CO_2H = 1:10$, v/v) before the polyfluoroarene was added. At least partial ionization of the sulphonate would be expected in solution, giving the highly electrophilic trifluoromethanesulphonatomercuric ion [reaction (5); $X = CF_3SO_3$].

$$HgX_2 \rightleftharpoons HgX^+ + X^- \qquad (5)$$

Greater ionization (5) when $X = CF_3SO_3$ than when $X = CF_3CO_2$ and/or greater electrophilicity for $HgO_3SCF_3^+$ than $HgO_2CCF_3^+$ would account for the greater reactivity of mercuric trifluoromethanesulphonate than mercuric trifluoroacetate. Mercuration of pentafluorobenzene with mercuric trifluoroacetate in either trifluoroacetic acid or aqueous trifluoroacetic acid ($H_2O:CF_3CO_2H = 1:10$, v/v) gave the same yield (Table 1) in the absence of trifluoromethanesulphonic acid. Thus, the water added to dissolve precipitated mercuric trifluoromethanesulphonate does not appear to have a significant effect independent of the addition of trifluoromethanesulphonic acid. This differs from the mercuration of benzene [17], where added water accelerates the reaction. However, all the present reaction mixtures contained some water, formed during the 'in situ' preparation of mercuric trifluoroacetate from mercuric oxide (cf. [17]).

Reaction of mercuric trifluoromethanesulphonate with 2,2'-bipyridyl gave tris(2,2'-bipyridyl)mercury(II) trifluoromethanesulphonate hydrate. Infrared bands of free 2,2'-bipyridyl [18] at 1582 and 1560 [ν(CC)], 992 [ring breathing] and 403 cm^{-1} [out of plane ring deformation] are shifted to higher frequencies, with splitting of the ν(CC) modes, in the spectrum of the complex (Experimental Section), as expected [18] for coordinated 2,2'-bipyridyl. The ^1H NMR spectrum of the complex shows no evidence of free ligand, though fast exchange between the ligand and a complex species cannot be excluded. The molar conductances [168 S cm^2 mol^{-1} in acetone (concn. : 2.00×10^{-3} mol dm^{-3}); 165 S cm^2 mol^{-1} in nitromethane (concn.: 1.11×10^{-3} mol dm^{-3})] are indicative [19] of a 2:1 electrolyte. These data are consistent with the presence of $[Hg(bpy)_3]^{2+}$, a species apparently not previously identified in solid complexes, though $[Hg(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) is known [20]. However, more sulphur-oxygen stretching frequencies are observed (Experimental Section) than expected for free trifluoromethanesulphonate ions, though the lowering of symmetry could arise from hydrogen bonding to water rather than from coordination of the sulphonate groups.

(b) Polyfluoroarylmercuric Chlorides

Identification of the polyfluoroarylmercuric chlorides generally followed readily from analytical and spectroscopic data (Experimental Section). The polyfluoroarene reactants have either one possible substitution position or equivalent positions, except for 1-bromo-2,4,5-trifluorobenzene. In this case, the product was identified as 3-bromo-2,5,6-trifluorophenylmercuric chloride (A) rather than 2-bromo-3,5,6-trifluorophenylmercuric chloride (B) by comparison of the calculated fluorine chemical shifts* with the observed values [A: Calcd.: 89.6 (F2), 112.2 (F6), 135.5 (F5) ppm upfield of $CFCl_3$. Observed: 91.2 (F2), 115.7 (F6), 137.8 (F5) ppm. B: Calcd.: 106.8 (F3), 118.2 (F6), 129.4 (F5) ppm]. The validity of the substituent chemical shifts can be seen by comparing calculated and found chemical shifts for 3-bromo-2,4,6-trifluorophenylmercuric chloride [calcd.: 81.4 (F2), 88.7 (F6), 97.8 (F4) ppm. Observed: 84.1 (F2), 90.9 (F6), 99.6 (F4) ppm]. The identity of A was confirmed by the proton chemical shift, which is substantially downfield from values for a hydrogen *ortho* to two fluorines, e.g. in 3-bromo-2,4,6-trifluorophenylmercuric chloride and 2,4,6-trifluorophenylmercuric chloride (Experimental Section). This is consistent with a bromine *ortho* to

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[*] Based on reported substituent chemical shifts [21] and values obtained from the ^{19}F NMR spectra of C_6F_5HgCl and the isomeric HC_6F_4HgCl derivatives (Experimental Section).

hydrogen. In addition, the $^{199}Hg-^{19}F$ coupling constants indicated that two fluorines are ortho to mercury. The preferred substitution position in 1-bromo-2,4,5-trifluorobenzene can be explained both by steric effects and by partial rate factors derived from mercuration of monohalogenobenzenes [22].

Full analyses of the ^{19}F NMR spectra are being made and will be reported later. Any difficulties with the assignments of the chemical shifts (Experimental Section) were generally resolved by use of substituent chemical shifts. However, in the case of 4-(2',3',5',6'-tetrafluorophenyl)-2,3,5,6-tetrafluorophenylmercuric chloride, this did not provide a sufficiently firm basis for distinguishing the resonances of F3, 5 from those of F2', 3', 5', 6', but the latter were readily recognized by the absence of mercury satellites.

The melting point of 2,3,5,6-tetrafluoro-4-methoxyphenylmercuric chloride (180-182°) was considerably higher than previously reported (138-139° [1]), when the compound was prepared by exchange between bis(2,3,5,6-tetrafluoro-4-methoxyphenyl)mercury and mercuric chloride. The melting point of the earlier sample has been confirmed, but the mixed melting point with the present product was much higher (178-182°). No significant differences could be detected between the infrared spectra of the two products.

The mercury-chlorine stretching frequencies of the polyfluoroarylmercuric chlorides are listed in Table 2. Assignments were often straightforward, there being only one intense band in the relevant region (360-320 cm^{-1}). In most other cases, comparison of the spectrum with that of the corresponding diorganomercurial enabled ν(Hg-Cl) to be recognized. However, a choice between bands of 2,3,4,5-tetrafluorophenylmercuric chloride at 343 and 332 cm^{-1} could not be made, since the one band of bis(2,3,4,5-tetrafluorophenyl)mercury between 360 and 320 cm^{-1} is at 338 cm^{-1}. As concluded earlier [23] for a range of hydrocarbon arylmercuric chlorides, no meaningful correlation can be made between the ν(Hg-Cl) frequencies and the nature of the substituents. For example, there is no common structural feature in the polyfluoroaryl groups ($\underline{p}$-$H_2NC_6F_4$, $\underline{m}$-$HO_2CC_6F_4$, 3-Br,5-HC_6F_3, and 3-Br,4H-C_6F_3) giving the lowest mercury-chlorine stretching frequencies. However, the values for the polyfluoroarylmercuric chlorides are generally higher than those of hydrocarbon arylmercuric chlorides (331-322 cm^{-1} [23]), possibly due to strengthening of the Hg-Cl bond by the electron withdrawing effect of the fluorocarbon groups. Other electron withdrawing groups cause an increase in ν(Hg-Cl) frequencies, e.g. values of 357 and 345 cm^{-1} are observed for C_6Cl_5HgCl [24] and PhC≡CHgCl [23], respectively.

TABLE 2. MERCURY-CHLORINE STRETCHING FREQUENCIES OF SOME POLYFLUOROARYLMERCURIC CHLORIDES

Compound	ν(Hg-Cl) cm^{-1}	Compound	ν(Hg-Cl) cm^{-1}
C_6F_5HgCl [a]	344	*m*-BrC_6F_4HgCl	344
p-$MeOC_6F_4HgCl$ [b]	356, 345	*o*-BrC_6F_4HgCl	342
p-MeC_6F_4HgCl	346	*p*-HOC_6F_4HgCl	346
p-HC_6F_4HgCl	350	*p*-$H_2NC_6F_4HgCl$	333
m-HC_6F_4HgCl	346	*m*-$HO_2CC_6F_4HgCl$	337
o-HC_6F_4HgCl	343 or 332	*p*-(*p*-$HC_6F_4)C_6F_4HgCl$	348
m-$O_2NC_6F_4HgCl$	347	3,5-$H_2C_6F_3HgCl$	344
o-$O_2NC_6F_4HgCl$	349	C_6HBrF_3HgCl [c]	332
p-BrC_6F_4HgCl	349	C_6HBrF_3HgCl [d]	337

[a] From Ref. [23]. [b] From Ref. [1]. [c] 3-Bromo-2,4,6-trifluorophenylmercuric chloride. [d] 3-Bromo-2,5,6-trifluorophenylmercuric chloride.

(c) Preparation of Bis(polyfluorophenyl)mercurials

Treatment of representative crude polyfluorophenylmercuric trifluoromethanesulphonates with aqueous methanolic potassium bromide at room temperature resulted in rapid symmetrization to give the corresponding bis(polyfluorophenyl)mercury compounds.

$$2RHgO_3SCF_3 + 4Br^- \longrightarrow R_2Hg + HgBr_4^{2-} + 2CF_3SO_3^- \qquad (6)$$

Fairly precise control of the reaction conditions appears to be needed, since changing the solvent composition in the reaction of 2,3,5,6-tetrafluorophenylmercuric trifluoromethanesulphonate with bromide ions (see Experimental Section) led to the isolation of the corresponding organomercuric bromide.

$$p\text{-}HC_6F_4HgO_3SCF_3 + Br^- \longrightarrow p\text{-}HC_6F_4HgBr + CF_3SO_3^-$$

The present symmetrization conditions are much milder than those [25a] required for rearrangement of hydrocarbon monoarylmercurials with halide ions (use of the more nucleophilic iodide ions/boiling solvents/longer reaction times).

Identification of the diorganomercurials by analysis and spectroscopic data was straightforward and only a few points require comment. Bis(4-amino-2,3,5,6-tetrafluorophenyl)mercury was isolated in two different crystalline forms, which showed minor but significant differences between their infrared spectra (Experimental Section). Use of petroleum ether (b.p.

100-120°) for recrystallization of bis(pentafluorophenyl)mercury resulted in isolation of the low melting form of the compound, previously obtained [26, 27] by sublimation of the mercurial. As reported [26, 27], this form reverted to the more common form on standing. Recrystallization from hexane [28] or petroleum ether (b.p. <40°) [29] gives samples with the normal melting point. In addition to the expected bis(2,3,5,6-tetrafluorophenyl)mercury, symmetrization of 2,3,5,6-tetrafluorophenylmercuric trifluoromethanesulphonate yielded some 1,4-bis(2',3',5',6'-tetrafluorophenylmercuri)-2,3,5,6-tetrafluorobenzene. This was probably formed by cosymmetrization (7) of 2,3,5,6-tetrafluoro-4-methoxyphenylmercuric trifluoromethanesulphonate and an impurity of the dimercurated species, 1,4-bis(trifluoromethanesulphonatomercuri)-2,3,5,6-tetrafluorobenzene, and has previously been obtained [7] as a by-product from mercuration of 1,2,4,5-tetrafluorobenzene under alkaline conditions.

$$2\,\underline{p}\text{-}HC_6F_4HgO_3SCF_3 + \underline{p}\text{-}(CF_3SO_3Hg)_2C_6F_4 + 8\,Br^- \longrightarrow$$
$$\underline{p}\text{-}(\underline{p}\text{-}HC_6F_4Hg)_2C_6F_4 + 2\,HgBr_4^{2-} + 4\,CF_3SO_3^- \qquad (7)$$

Formation of unsymmetrical diorganomercurials by cosymmetrization has seldom been achieved [25b].

Symmetrization was also observed on heating several polyfluorophenylmercuric trifluoromethanesulphonates in aqueous methanol [reaction (3); R = $\underline{p}$-MeOC_6F_4, $\underline{p}$-MeC_6F_4, $\underline{o}$-BrC_6F_4, or $\underline{o}$-$O_2NC_6F_4$]. The same reaction was observed, though not on preparative scale, on dissolution of 2,3,5,6-tetrafluoro-4-methoxyphenylmercuric trifluoromethanesulphonate in acetone [section (a)], and a related rearrangement of arylthallium bistrifluoroacetates into diarylthallium trifluoroacetates in boiling acetone is known [30]. For the present compounds, symmetrization with bromide ions [reaction (6)] was more convenient than use of reaction (3).

(d) General Conclusions

The need for forcing conditions in the mercuration of most polyfluoroarenes has hitherto restricted use of this method in the synthesis of polyfluoroarylmercurials. Use of trifluoromethanesulphonic acid has transformed mercuration of polyfluoroarenes into a simple, convenient, and general synthetic route, and the products can be isolated as either polyfluoroarylmercuric chlorides or bis(polyfluoroaryl)mercurials. Accordingly, mercuration in the presence of trifluoromethanesulphonic acid should become the method of choice for the synthesis of most polyfluoroarylmercurials. The range of polyfluoroarenes available commercially for use in mercuration reactions is much wider than the selection of halogenopolyfluorobenzenes available for the synthesis of Grignard reagents [31].

Experimental

Microanalyses were by the Australian Microanalytical Service, Melbourne. Mercury was analysed by the gravimetric method using hydrogen sulphide [32]. Infra-red spectra of compounds as Nujol and hexachlorobutadiene mulls (4000–400 or 50 cm^{-1}) were recorded with a Perkin-Elmer 180 instrument. Sulphonate complexes were examined using silver chloride plates, since they can undergo group exchange with alkali metal halide plates [12]. Polythene plates were used for far infrared measurements. When 2,3,5,6-tetrafluoro-4-methoxyphenylmercuric chloride was examined using caesium iodide plates, the ν(Hg-Cl) absorption was not observed, presumably owing to anion exchange with the plates. ^{19}F NMR and ^{1}H NMR spectra of compounds (in $CDCl_3$ solution unless stated otherwise) were recorded with a Brüker WH-90 instrument, the fluorine resonances being given in ppm upfield of internal trichlorofluoromethane and proton resonances in ppm downfield of internal tetramethylsilane. Mass spectra were recorded with AEI MS 30 or VG micromass instruments, the samples being introduced by direct evaporation. Each m/e value listed represents the most intense peak in a cluster having the correct isotope pattern for the assignment given. Isotope patterns were calculated with the FORTRAN program BMASROS [33]. Conductances were measured at *ca.* 19° with a Wayne-Kerr B221A bridge using a cell of standard design fitted with shiny platinum electrodes.

Reagents

Polyfluoroarenes and trifluoroacetic acid were obtained from Bristol Organics except for 2,3,5,6-tetrafluoroaniline (Pierce) and 2,3,4,6-tetrafluorobenzoic acid, which was provided by R. J. Phillips of this department (synthesis [34]). Mercuric oxide (red) was from May and Baker and trifluoromethanesulphonic acid was from 3M.

General Preparative Methods

(a) Mercuration Reactions

Mercuric oxide (10 mmol) was dissolved in trifluoroacetic acid (10 ml) and trifluoromethanesulphonic acid (1.8 ml, 20 mmol) was added. The resulting white precipitate was dissolved by the dropwise addition of water (*ca.* 1 ml), and the polyfluoroarene (Table 1) (12 mmol) was added. The reactions were considered to be complete when a small sample of the reaction mixture gave no precipitate of mercuric oxide when added to an excess of aqueous sodium hydroxide. Reaction conditions are listed in Table 1, and any modifications of this procedure are included with the characterization of products (below).

(b) Polyfluoroarylmercuric chlorides

The reaction mixtures from (a) were reduced to dryness under vacuum and the resulting residues were dissolved in methanol (5 ml). Concentrated hydrochloric acid (2 ml) was added and dilution of the mixture to ca. 100 ml with water precipitated the crude products, which were collected and dried (vacuum/P_2O_5). Purification was usually effected by a single recrystallization from hexane. Yields of the pure compounds are given in Table 1. Variations from the general method are given with the individual compounds (see later).

(c) Bis(polyfluoroaryl)mercurials

The reaction mixtures from (a) were reduced to dryness under vacuum and the resulting residues were dissolved in methanol (50 ml). Potassium bromide (10 gm) in 50 ml of aqueous methanol (1:1, v/v) was added and the whole mixture was poured into 500-700 ml of cold water, precipitating the crude products which were collected and dried (vacuum/P_2O_5). Yields of the pure compounds are given in Table 1. Details of purification procedures, and variations from the general method are given with the individual compounds (see below).

Characterization of Products

All compounds were obtained as white crystals unless indicated otherwise.

2,3,5,6-Tetrafluoro-4-methoxyphenylmercuric chloride. - m.p. 180-182°, lit. [1] m.p. 138-139° (Found: C, 19.9; H, 1.3; F, 18.8. $C_7H_3ClF_4HgO$ calcd.: C, 20.2; H, 0.7; F, 18.3%). The infra-red spectrum was in agreement with that reported [1]. Mass spectrum: 416 (M^+). ^{19}F NMR spectrum: 121.3, m (2F, F2, 6), 154.9, m (2F, F3, 5). ^1H NMR spectrum: 4.11, t (J 1.6 Hz, OCH_3).

2,3,5,6-Tetrafluoro-4-methoxyphenylmercuric trifluoromethanesulphonate (nc). - 2,3,5,6-Tetrafluoroanisole was mercurated as described (a). The reaction mixture was reduced to half-volume under vacuum and the resulting white crystalline precipitate was redissolved by gentle warming (60°). On cooling, the required product crystallized and was collected and dried at 120° for 24 h under vacuum (yield 40%), m.p. 183° (dec.) (Found: S, 5.8.

$C_8H_3F_7HgO_4S$ calcd.: S, 6.1%). The compound was slightly hygroscopic and was subsequently handled in a glove-bag under dry nitrogen. Infra-red absorption (4000-650 cm^{-1}): 3200w (vbr), 1632w, 1462s (br), 1340s, $\nu(SO_2)$ [11-13], 1210s (br), $\nu(CF_3)$ [13], 1132s, $\nu(SO_2)$ [11-13], 1107s, 1015m, $\nu(SO)$ [11-13], 969s, 805m, 717w cm^{-1}. The mass spectrum was identical with that of bis(2,3,5,6-tetrafluoro-4-methoxyphenyl)mercury, probably owing to thermal rearrangement. The ^{19}F NMR spectrum was time-dependent and was interpreted as arising from a mixture of 2,3,5,6-tetrafluoro-4-methoxyphenylmercuric trifluoromethanesulphonate, bis(2,3,5,6-tetrafluoro-4-methoxyphenyl)mercury and mercuric trifluoromethanesulphonate. Shortly after dissolution of the sample in perdeuteroacetone, the ^{19}F NMR spectrum was as follows: 77.6, s [3F, $C\underline{F}_3SO_3HgC_6F_4OCH_3$], 77.8, s [6F, $Hg(O_3SC\underline{F}_3)_2$], 119.5, m [2F, F2, 6 of $CF_3SO_3HgC_6F_4OCH_3$], 121.5, m [4F, F2, 6 of $(CH_3OC_6F_4)_2Hg$], 156.5, m [6F, F3, 5 of $(CH_3OC_6F_4)_2Hg$ and $CF_3SO_3HgC_6F_4OCH_3$]. The integration was consistent with equimolar amounts of the three components. ^1H NMR spectrum [$(CD_3)_2CO$]: 4.10, t (J 1.2 Hz, $OC\underline{H}_3$). After *ca.* 10 min the ^{19}F NMR spectrum had simplified as follows: 77.9, s [6F, $Hg(O_3SC\underline{F}_3)_2$], 121.4, m [4F, F2, 6 of $(CH_3OC_6F_4)_2Hg$], 156.2, m [4F, F3, 5 of $(CH_3OC_6F_4)_2Hg$]. *Conversion into the chloromercuri derivative.* 2,3,5,6-Tetrafluoro-4-methoxyphenylmercuric trifluoromethanesulphonate (0.5 gm) was dissolved in methanol (2 ml) and was *immediately* treated with concentrated hydrochloric acid (1 ml). Dilution with water (100 ml) precipitated 2,3,5,6-tetrafluoro-4-methoxyphenylmercuric chloride (100%), m.p. 178-180° (i.r. identification). *Partial symmetrization with water.* 2,3,5,6-Tetrafluoro-4-methoxyphenylmercuric trifluoromethanesulphonate was washed with cold water giving an insoluble solid, m.p. 120-160° (Found: S, 2.2%), the infra-red spectrum of which was consistent with an impure sample of bis(2,3,5,6-tetrafluoro-4-methoxyphenyl)mercury. Addition of strong sodium hydroxide solution to the washings gave a precipitate of yellow mercuric oxide.

2,3,5,6-Tetrafluoro-4-methylphenylmercuric chloride (nc). - m.p. 159-160° (Found: C, 21.2; H, 0.8; F, 19.3. $C_7H_3ClF_4Hg$ calcd.: C, 21.1; H, 0.8; F, 19.3%). Infra-red absorption: 3010w, 2960w, 2935m, 2860w, 1460vs (br), 1378s, 1256s, 1110s, 1059s, 1030m, 898vs, 799m, 725w (br), 585m, 579m, 490w, 346m, 224w, 174w, 120m, 100m, 60w (br) cm^{-1}. Mass spectrum: 400 (M^+). ^{19}F NMR spectrum: 122.4, m (2F, F2, 6), 141.3, m (2F, F3, 5). ^1H NMR spectrum: 2.31, t (J 2.2 Hz, $C\underline{H}_3$).

2,3,4,6-Tetrafluorophenylmercuric chloride. - m.p., 143-144°, lit. [6] m.p., 143-144°. The infra-red spectrum was in agreement with that reported [6]. Mass spectrum: 386 (M^{+}). ^{19}F NMR spectrum: 95.5, m (1F, F6), 113.3, m (1F, F2), 128.7, m (1F, F4), 163.5, m (1F, F3). ^{1}H NMR spectrum: 6.88, m (H5).

2,3,5,6-Tetrafluorophenylmercuric chloride. - The initial mercuration was carried out using a three-fold excess of 1,2,4,5-tetrafluorobenzene. The product obtained by procedure (b) had m.p., 187-188°, lit. [7] m.p., 186-188°. The infra-red spectrum was in agreement with that reported [7]. Mass spectrum: 386 (M^{+}). The ^{19}F NMR spectrum: 121.1, m (2F, F2, 6), 136.5, m (2F, F3, 5) showed satisfactory agreement with reported data (acetone solvent) [7]. ^{1}H NMR spectrum: 7.08, m (H4). The resonance in acetone (7.42, m) agreed with the reported [7] value.

2,3,4,5-Tetrafluorophenylmercuric chloride. - The crude product from procedure (b) was heated in a sublimer at 100° for 2 h. under vacuum. A sublimate of the required compound m.p. 155-156°, lit. [6] m.p. 152-153°, was collected. The infra-red spectrum was in agreement with that reported [6]. Mass spectrum: 386 (M^{+}). The ^{19}F NMR spectrum: 118.7, m (1F, F2), 137.7, m (1F, F5), 153.2, m (1F, F3 or F4), 153.4, m (1F, F3 or F4) showed reasonable agreement with reported [27] values (in acetone). ^{1}H NMR spectrum: 7.00, m (H6); reported [6] value [(CD$_3$)$_2$CO]: 7.53, m. Sublimation at higher temperatures and for longer periods gave products contaminated with the less volatile 1,2-bis(chloromercuri)-3,4,5,6-tetrafluorobenzene, which was also obtained [infra-red identification [6], m.p. > 275°, lit. [6] ca. 300° (dec.)] as the residue after sublimation.

Pentafluorophenylmercuric chloride. - m.p. 166-167°, lit. [35] m.p. 165°. The infra-red spectrum was in agreement with that reported [35]. Mass spectrum: 404 (M^{+}). ^{19}F NMR spectrum: 119.2, m (2F, F2, 6), 149.7, m (1F, F4), 158.6, m (2F, F3, 5).

2,3,4,6-Tetrafluoro-5-nitrophenylmercuric chloride (nc). - The compound was obtained as pale yellow crystals, m.p. 157-158° (dec.) (Found: C, 16.7; F, 17.5. $C_6ClF_4HgNO_2$ calcd.: C, 16.8; F, 17.7%). Infra-red absorption: 1631m, 1609m, 1550sh, 1543s, $\nu_{as}(NO_2)$ [36], 1490s, 1444s, 1375m, 1349vs, $\nu_{s}(NO_2)$ [36], 1096 and 1092s, 943s, 837m, 781m, 750w, 705m, 686m, 637w, 607w, 456w, 377 and 372w, 347m, 332m, 209w, 158w, 110m, 75m cm^{-1}. Mass spectrum: 431 (M^{+}). ^{19}F NMR spectrum: 102.3, m (1F, F6), 104.9, m (1F, F2), 134.3, m (1F, F4), 157.0, m (1F, F3).

2,3,4,5-Tetrafluoro-6-nitrophenylmercuric chloride (nc). - The mercuric oxide test (a) indicated that the mercuration was incomplete. The pure compound was obtained as pale yellow crystals, m.p. 141-142° (Found: C, 16.4; F, 17.8%). Infra-red absorption: 1625sh, 1610 and 1605m, 1530vs, $\nu_{as}(NO_2)$ [36], 1492s, 1455vs, 1358sh, 1330s, $\nu_{s}(NO_2)$ [36], 1284s, 1270sh, 1125s, 1049s, 919w, 813m, 776m, 759m, 748w, 580w, 475w, 368w, 349s, 340sh, 325w, 282w, 243w, 203m, 158w, 127m, 107s cm^{-1}. Mass spectrum: 431 (M^{+}). ^{19}F NMR spectrum: 111.9, m (1F, F2), 136.5, m (1F, F5), 140.3, m (1F, F3), 146.9, m (1F, F4).

4-Bromo-2,3,5,6-tetrafluorophenylmercuric chloride (nc). - m.p. 202-203° (Found: C, 15.6; F, 16.7. $C_6BrClHgF_4$ calcd.: C, 15.5; F, 16.4%). Infra-red absorption: 1618w, 1463vs, 1446sh, 1372m, 998w, 940s, 903w, 777m, 572w, 349m, 255w, 222w, 134w, 116m, 87m cm^{-1}. Mass spectrum: 464 (M^{+}). ^{19}F NMR spectrum: 119.1, m (2F, F2, 6), 130.6, m (2F, F3, 5).

3-Bromo-2,4,5,6-tetrafluorophenylmercuric chloride (nc). - m.p. 135.5-136° (Found: C, 15.6; F, 16.6%). Infra-red absorption: 1624m, 1610sh, 1586w, 1476vs, 1439s, 1358m, 1232 and 1215w, 1080m, 1069s, 1053 and 1048m, 880s, 760m, 730m, 713w, 679m, 643w, 608w, 458w, 386w, 344s, 325m, 247w, 220w, 190w, 146w(br), 106s(br), 74w(br) cm^{-1}. Mass spectrum: 464 (M^{+}). ^{19}F NMR spectrum: 90.5, m (1F, F2), 113.7, m (1F, F6), 121.2, m (1F, F4), 159.0, m (1F, F5).

2-Bromo-3,4,5,6-tetrafluorophenylmercuric chloride. - m.p. 136-136.5°, lit. [27] m.p. 130-133° (Found: C, 15.4; F, 16.5%). Infrared absorption: 1650sh, 1608m, 1540w, 1499s, 1442vs, 1356m, 1324m, 1263m, 1114m, 1100m, 1031m, 1014s, 823vs, 788m, 636w, 362w, 342s, 258w, 213w, 100m, 85sh cm^{-1}. Mass spectrum: 464 (M^{+}). ^{19}F NMR spectrum: 118.9, m (1F, F6), 124.2, m (1F, F3), 149.4, m (1F, F4), 152.4, m (1F, F5). Corresponding reported [37] values (solvent unspecified) are 117.9, 125.7, 152.7, 154.5.

2,3,5,6-Tetrafluoro-4-hydroxyphenylmercuric chloride (nc). - The crude compound from procedure (b) was recrystallized from hexane/acetone [52% yield; m.p. 211° (dec.)] and then from hexane/chloroform to give the pure compound (31%), m.p. 214° (dec.) (Found: C, 17.7; H, 0.5; F, 18.7. C_6HClF_4HgO calcd.: C, 18.0; H, 0.3; F, 19.0%). Infra-red absorption: 3600, 3400, and 3150m (vbr), $\nu(OH)$ [38a], 1642m, 1630sh, 1513m, 1490sh, 1476vs, 1360m (br), 1266m, 1103s, 1075m, 1040vw (br), 960sh, 948vs, 808w, 758w, 717w, 358m, 346m, 298w, 281w, 228w, 200w, 172w, 118m, 102m, 69w, 56w cm^{-1}. Mass spectrum: 402 (M^+). ^{19}F NMR spectrum: 121.7, m (2F, F2, 6), 160.3, m (2F, F3, 5). The corresponding values in acetone are 121.7, m and 160.2, m. ^1H NMR spectrum: $[(CD_3)_2CO]$: *ca.* 3.8, s(br), exchanges with D_2O, (OH), 7.5 and 8.5, w (impurity).

4-*Amino*-2,3,5,6-*tetrafluorophenylmercuric chloride (nc)*. - The reaction mixture from procedure (a) was evaporated to dryness under vacuum and the residue was dissolved in methanol (10 ml). Saturated potassium chloride solution was added until no further precipitate appeared. The crude compound was collected, dried (vacuum/silica gel), and recrystallized from toluene/ carbon tetrachloride, m.p. 183.5-184.5° (Found: C, 18.0; H, 0.6; N, 3.7; F, 18.7. $C_6H_2ClF_4HgN$ calcd.: C, 18.0; H, 0.5; N, 3.5; F, 19.0%). Infra-red absorption: 3450s, ν(NH) [38b], 3300 and 3190s (br), ν(NH) [38b], 1655vs, 1610s, 1500vs, 1471s, 1384w, 1363w, 1313w, 1264s, 1170s, 1099s, 995w, 915s, 798m, 730 and 716w, *ca.* 700w (br), 611w, 595m, 509 and 495m, 420w, 350m, 333s, 308w, 292w, 170w, 120s, *ca.* 85m(br) cm^{-1}. Mass spectrum: 401 (M^+). ^{19}F NMR spectrum: 123.1, m (2F, F2, 6), 159.9, m (2F, F3, 5). ^1H NMR spectrum: 5.38, s(br), exchanges with D_2O, (NH_2). The compound discolours on standing.

3-*Carboxy*-2,4,5,6-*tetrafluorophenylmercuric chloride (nc)*. - The initial mercuration [procedure (a)] was performed on a 5 mmol scale. The reaction mixture was cooled to room temperature and concentrated hydrochloric acid (1 ml) was added, precipitating the crude product. The solvent was removed under vacuum and the residue was mixed with cold water (5 ml). The insoluble solid was collected by filtration, dried (vacuum/silica gel), and recrystallized from toluene, m.p. 209-210° (Found: C, 19.6; H, 0.6; F, 17.2. $C_7HClF_4HgO_2$ calcd.: C, 19.6; H, 0.2; F, 17.7%). Infrared absorption: *ca.* 3000m (vbr), ν(OH) [38c], 1700s, $\nu_{as}(CO_2)$ [38c], 1625m, 1475s, 1400m, 1290sh, 1278m, 1220m, 1168 and 1150w, 1082s, 919m, 895sh, 795m, 720w, 707sh, 666m, 646w, 612w, 579w, 466 and 458m, 382m, 372w, 346m, 337s, 312m, 239m, 222m, 160w, 119m, 93m(br) cm^{-1}. Mass spectrum: 430 (M^+). ^{19}F NMR spectrum: $[(CD_3)_2CO]$: 93.0, m (1F, F2), 108.6, m (1F, F6), 132.3, m (1F, F4), 164.2, m (1F, F5). ^1H NMR spectrum $[(CD_3)_2CO]$: *ca.* 8.6, s(br), exchanges with D_2O, (COO*H*).

4-(2',3',5',6'-*Tetrafluorophenyl*)-2,3,5,6-*tetrafluorophenylmercuric chloride (nc)*. - The reaction mixture from procedure (a) was evaporated to dryness under vacuum and the residue was washed once with petroleum spirit (b.p. 60-80°) to remove any unreacted 2,2',3,3',5,5',6,6'-octafluorobiphenyl. The residue was then worked up according to procedure (b) to give the required compound, m.p. 241° (dec.) (Found: C, 27.2; H, 0.4; F, 28.5. $C_{12}HClF_8Hg$ calcd.: C, 27.0; H, 0.2; F, 28.5%). Infra-red absorption: 3085vw, 1609w, 1580w, 1516sh, 1499vs, 1451vs, 1401w, 1390w, 1366w, 1259w, 1229m, 1181s, 1129w, 963s, 941w, 922vs, 855 and 851m, 740w, 709m, 599w, 413w, 376w, 348m, 304w, 239w, 225w, 116m, 109sh, 71m cm^{-1}. Mass spectrum: 534 (M$^+$). ^{19}F NMR spectrum: 119.6, m (2F, F2, 6), 136.0, m (2F, F3, 5), 138.5, m (4F, F2', 3', 5' 6'). ^{1}H NMR spectrum[$(CD_3)_2CO$]: 7.84, m (H4').

2,4,6-Trifluorophenylmercuric chloride (nc). - m.p. 154-155° (Found: C, 19.3; H, 0.8; F, 15.3. $C_6H_2ClF_3Hg$ calcd.: C, 19.6; H, 0.6; F, 15.5%). Infra-red absorption: 3100w, 1655w, 1633m, 1600vs, 1575sh, 1509w, 1477m, 1416vs, 1399m, 1290m, 1160s, 1120 and 1115m, 1065w, 1035s, 1016vs, 1000s, 832vs, 724w(br), 693w, 610s, 587w, 569w, 509m, 363w, 344m, 328w, 316m, 216w, 184w, 132m, 105m, 60m cm^{-1}. Mass spectrum: 368 (M$^+$). ^{19}F NMR spectrum: 89.7, m (2F, F2, 6), 105.2, m (1F, F4). ^{1}H NMR spectrum: 6.76, m (H3, 5).

3-Bromo-2,4,6-trifluorophenylmercuric chloride (nc). - The crude product from procedure (b) was heated in a sublimer at 100° for 1 h under vacuum giving a sublimate of the required compound, m.p. 136.5-137° (Found: C, 16.2; H, 0.4; F, 12.7. $C_6HBrClF_3Hg$ calcd.: C, 16.2; H, 0.2; F, 12.8%). Infra-red absorption: 3085w, 1690w, 1653w, 1594m, 1576s, 1454m, 1411m, 1365vs, 1343w, 1299w, 1147m, 1088w, 1043s, 1035m, 1020vs, 845vs, 724w(br), 705w, 682m, 610m, 593m, 580w, 553w, 352w, 343w, 332s, 293w, 249w, 218w, 190w, 162w, 106s, 74m cm^{-1}. Mass spectrum: 446 (M$^+$). ^{19}F NMR spectrum: 84.1, m (1F, F2), 90.9, m (1F, F6), 99.6, m (1F, F4). ^{1}H NMR spectrum: 6.88, m (H5).

3-Bromo-2,5,6-trifluorophenylmercuric chloride (nc). - m.p. 124-125° (Found: C, 16.5; H, 0.2; F, 13.1%). Infra-red absorption: 3090w, 1712w, 1660w(br), 1602w, 1460vs(br), 1409w, 1400w, 1350w, 1313w, 1278w, 1260w, 1211m, 1194s, 1187s, 1148w, 1025w, 1015w, 900w, 872s, 859s, 808w, 760m, 700m, 662m, 459w, 397w, 337s, 296w, 258w, 206w, 184w, 152w, 115s, 100m, 75m cm^{-1}. Mass spectrum: 446 (M$^+$). ^{19}F NMR spectrum: 91.2, m (1F, F2), 115.7, m (1F, F6), 137.8, m (1F, F5). ^{1}H NMR spectrum: 7.40, m (H4).

Bis(2,3,5,6-tetrafluoro-4-methoxyphenyl)mercury. - Recrystallization from petroleum spirit (b.p. 100-120°) gave needles, m.p. 154°, lit. [39] m.p.

153-154°. The infra-red spectrum was in agreement with that reported [6]. Mass spectrum: 560 (M^{+}). The ^{19}F NMR spectrum: 121.9, m (4F, F2, 6), 155.7, m (4F, F3, 5) was in good agreement with the reported [6] spectrum (acetone solvent). ^{1}H NMR spectrum: 4.10, t (J 1.5 Hz, OC$\underline{H}_3$).

Bis(2,3,5,6-tetrafluoro-4-methylphenyl)mercury (nc). - Recrystallization from petroleum spirit (b.p. 100-120°) gave needles, m.p. 158-158.7° (Found: C, 32.1; H, 1.2; F, 28.8. $C_{14}H_6F_8Hg$ calcd.: C, 31.9; H, 1.1; F, 28.5%). Infra-red absorption: 2945 and 2925w, 2860w, 1642w, 1588w, 1455vs(br), 1385m, 1375s, 1351s, 1242vs, 1114s, 1050s, 1020s, 896vs, 796s, 720w, 578s, 486m cm^{-1}. Mass spectrum: 528 (M^{+}). ^{19}F NMR spectrum: 123.2, m (4F, F2, 6), 142.3, m (4F, F3, 5). ^{1}H NMR spectrum: 2.31, t (J 2.2 Hz, C$\underline{H}_3$).

Bis(pentafluorophenyl)mercury. - Recrystallization from petroleum spirit (b.p. 100-120°) gave needles melting at 116° immediately after isolation but at 138-139° on standing, lit. [35] m.p. 142°. The infra-red spectrum was in agreement with that reported [35]. Mass spectrum: 536 (M^{+}). ^{19}F NMR spectrum: 120.2, m (4F, F2, 6), 150.9, m (2F, F4), 159.4, m (4F, F3, 5). Corresponding reported [27, 40] values: 117.5, 148.4 and 156.8 ($CDCl_3$); 119.2, 154.7 and 161.3 (CH_3OH).

Bis(2,3,5,6-tetrafluorophenyl)mercury. After mercuration (a) using mercuric oxide (10 mmol) and 1,2,4,5-tetrafluorobenzene (30 mmol), the crude product from procedure (c) was sublimed under vacuum at 110°, giving the required mercurial (53%) which was recrystallized from petroleum spirit (b.p. 40-60°), m.p. 149.5-150°, lit. [7, 29] m.p. 146-147°; 149-150°. The infra-red, ^{19}F NMR and ^{1}H NMR spectra were in agreement with those reported [7]. Mass spectrum: 500 (M^{+}). The residue from the sublimation (m.p. > 300°) was recrystallized from chloroform/hexane giving 1,4-bis-(2', 3', 5', 6'-tetrafluorophenylmercuri)-2,3,5,6-tetrafluorobenzene (infra-red identification [7]). Mass spectrum: 848 (M^{+}). Modification of procedure (c) by dissolution of the residue from (a) in 5 ml (not 50 ml) of methanol gave 2,3,5,6-tetrafluorophenylmercuric bromide (yield 79%), which was recrystallized from petroleum spirit (b.p. 80-100°) and obtained in 42% yield, m.p. 181-182°, lit. [41] m.p. 179-181° (Found: C, 17.1; H, 0.2; F, 17.5. C_6HBrF_4Hg calcd.: C, 16.8; H, 0.2; F, 17.7%). Infra-red absorption: 3105 and 3075w, 1611sh, 1600s, 1473vs(br), 1431sh, 1362s, 1271m, 1231s, 1169s, 1122w, 1000w, 981w, 930m, 898s, 865m, 849s, 711s, 695m, 665m, 312m, 247m, ν(HgBr), 215m, 116sh, 108s cm^{-1}. Mass spectrum: 430 (M^+). ^{19}F NMR spectrum [$(CD_3)_2CO$]: 120.5, m (2F, F2, 6), 138.3, m (2F, F3, 5). ^1H NMR spectrum [$(CD_3)_2CO$]: 7.42, m (H4). The filtrate from the above recrystallization gave a mixture of 2,3,5,6-tetrafluorophenylmercuric bromide and bis(2,3,5,6-tetrafluorophenyl)mercury (i.r. identification) when evaporated to dryness.

Bis(2,3,4,6-*tetrafluoro*-5-*nitrophenyl)mercury (nc)*. - After mercuration (a) using a two-fold excess of mercurating agent, procedure (c) gave the crude diorganomercurial in quantitative yield (based on 1,2,3,5-tetrafluoro-4-nitrobenzene). Recrystallization from benzene/petroleum spirit (b.p. 100-120°) gave pale yellow plates, m.p. 142.5-143.5° (Found: C, 24.9; F, 26.2. $C_{12}F_8HgN_2O_4$ calcd.: C, 24.5; F, 25.8%). Infra-red absorption: 1665sh, 1628s, 1608s, 1540vs, $\nu_{as}(NO_2)$ [36], 1482vs, 1446s, 1385sh, 1365s, 1347vs, $\nu_s(NO_2)$ [36], 1333sh, 1290w, 1238w, 1081s, 937s, 833s, 779m, 749w, 702m, 693m, 637w, 606w, 578w, 470 and 456w, 381m, 341w, 300w, 215s, 180s, 132w, 100w cm^{-1}. Mass spectrum: 590 (M^+). ^{19}F NMR spectrum: 102.7, m (2F, F6), 105.0, m (2F, F2), 135.1, m (2F, F4), 157.8, m (2F, F3).

Bis(2,3,4,5-*tetrafluoro*-6-*nitrophenyl)mercury*. - Recrystallization from benzene gave pale yellow needles, m.p. 202-203°, lit. [6] m.p. 200-202° (Found: C, 24.6; F, 25.4%). The infra-red (4000-400 cm^{-1}) and ^{19}F NMR [$(CD_3)_2CO$] spectra were in agreement with those reported [6]. Infra-red spectrum (525-50 cm^{-1}): 474w, 279w, 215m, 185m, 140m, *ca.* 90w(br) cm^{-1}. Mass spectrum: 590 (M^+).

Bis(4-*bromo*-2,3,5,6-*tetrafluorophenyl)mercury*. - Recrystallization from petroleum spirit (b.p. 100-120°) gave flakes, m.p. 237.5-238.5° (Found: C, 22.0; F, 22.9. $C_{12}Br_2F_8Hg$ calcd.: C, 22.0; F, 23.2%). Infra-red absorption: 1612m, 1455 and 1438vs(br), 1367s, 1275w, 1236s, 1020w, 999 and 979w, 946vs, 898s, 774s, 721w, 580m, 499w, 439w cm^{-1}. Mass spectrum: 658 (M^+). ^{19}F NMR spectrum: 119.3, m (4F, F2, 6), 131.5, m (4F, F3, 5). Reference has previously been made to this mercurial [42], but the preparation and properties have not been reported.

Bis(3-*bromo*-2,4,5,6-*tetrafluorophenyl)mercury*. - Recrystallization from petroleum spirit (b.p. 60-80°) gave prisms, m.p. 130.5-131.5° (Found: C, 22.3; F, 23.1). Infra-red absorption: 1621m, 1612sh, 1587m, 1473vs, 1435vs, 1350s, 1230m, 1219s, 1072s, 1052s, 817s, 730m, 718m, 682m, 649w, 459w, 392w, 283w, 248 and 244w, 204s, 160w, 121m cm^{-1}. Mass spectrum: 658 (M^+). ^{19}F NMR spectrum: 91.3, m (2F, F2), 115.0, m

(2F, F6), 122.5, m (2F, F4), 159.9, m (2F, F5). Reference has previously been made to this mercurial [42] , but the preparation and properties have not been reported.

Bis(2-*bromo*-3,4,5,6-*tetrafluorophenyl)mercury*. - Recrystallization from petroleum spirit (b.p. 60-80°) gave prisms, m.p. 157-157.5°, lit. [43] m.p. 160-162° (Found: C, 22.2; F, 23.4%). Infra-red absorption: 1658w, 1622m, 1603m, 1545w, 1530w, 1492s, 1441vs(br), 1351s, 1325s, 1310 and 1300sh, 1268w, 1252w, 1165w, 1095s, 1039m, 1017s, 833vs, 796w, 782s, 722sh, 639w, 475 and 470w, 361s, 291w, 261w, 231vs, 216sh, 160m, 106m cm^{-1}. Mass spectrum: 658 (M^+). ^{19}F NMR spectrum: 119.8, m (2F, F6), 126.3, m (2F, F3), 150.8, m (2F, F4), 153.6, m (2F, F5). Corresponding reported [43] values (solvent unspecified): 119.4, 127.1, 153.2, 155.1.

Bis(2,3,5,6-*tetrafluoro*-4-*hydroxyphenyl)mercury*. - Recrystallization from toluene gave plates, m.p. > 300°, lit. [39] m.p. > 400° (Found: C, 26.6; H, 0.6; F, 28.5. $C_{12}H_2F_8HgO_2$ calcd.: C, 27.2; H, 0.4; F, 28.6%). Infra-red absorption: 3665w, 3590w, *ca.* 3330s(vbr), ν(OH) [38a] , 1636s, 1613s, 1552w, 1506s, 1475vs(br), 1390s, 1358s, 1331sh, 1275s, 1203sh, 1073s, 994w, 946s, 807m, 750 and 740w, 716w, 651w, 623w, 589w, 560w(br), 491w, 447w, 371w, 355w, 297w, 283m, 235w, 200s, 144w, 127w, *ca.* 80w(br) cm^{-1}. Mass spectrum: 532 (M^+). ^{19}F NMR spectrum [$(CD_3)_2CO$]: 122.4, m (4F, F2, 6), 160.7, m (4F, F3, 5). ^1H NMR spectrum [$(CD_3)_2CO$]: 3.1, s(br), exchanges with D_2O, (OH).

Bis(4-*amino*-2,3,5,6-*tetrafluorophenyl)mercury (nc)*. - Recrystallization from benzene gave the compound in two crystalline forms, which were separated by hand picking. α-Form (needles), m.p. 262-263° (Found: C, 27.3; H, 0.8; F, 28.3. $C_{12}H_4F_8HgN_2$ calcd.: C, 27.3; H, 0.8; F, 28.7%). Infra-red absorption: 3477m and 3392m, ν(NH) [38b] , 1653s, 1614m, 1494s, 1465vs, 1365s, 1310w, 1262s, 1176m, 1091s, 1082sh, 907s, 800m, 717m, 655m(br), 610m, 585sh, 422w, 350m, 284m, 195s, 140w cm^{-1}. Mass spectrum: 530 (M^+). ^{19}F NMR spectrum (C_5D_5N): 122.2, m (4F, F2, 6), 158.8, m (4F, F3, 5). ^1H NMR spectrum (C_5D_5N): 6.67, s, exchanges with D_2O, (NH_2). β-Form (prisms), m.p. 257-258° (Found: C, 27.6; H, 0.9; F, 28.4%). Infra-red absorption: 3490m and 3399s, ν(NH) [38b] , 1649s, 1613 and 1599m, 1500s, 1469vs, 1362s, 1310w, 1267s, 1162m, 1099s, 1085sh, 910s, 810w, 719w, *ca.* 640w(br), 615, 610 and 602w cm^{-1}. Mass spectrum: 530 (M^+). The NMR spectra (^{19}F, ^1H) were identical with those of the α-form. The compound discolours upon standing.

Symmetrization in aqueous methanol

The polyfluoroarenes were mercurated as described (a) and the reaction mixtures were reduced to dryness under vacuum. The residues were then dissolved in 500-1000 ml of aqueous methanol and the solutions were boiled down to crystallization. When cool, the diorganomercurials were filtered off and dried over P_2O_5 under vacuum. All products had infra-red spectra identical with those of authentic samples prepared by procedure (c). *Bis*(2,3,5,6-*tetrafluoro*-4-*methoxyphenyl)mercury*. The compound was obtained in 68% yield, m.p. 153-154°, mixed melting point (with an authentic sample), 153-154°. *Bis*(2,3,5,6-*tetrafluoro*-4-*methylphenyl)-mercury*. The crude compound (73% yield) was recrystallized from benzene/ petroleum spirit (b.p. 100-120°), yield 42%, m.p., 158-159°. *Bis*(2-*bromo*-3,4,5,6-*tetrafluorophenyl)mercury*. The crude compound (42% yield) was recrystallized from petroleum spirit (b.p. 40-70°), yield 30%, m.p. 157-158°. *Bis*(2,3,4,5-*tetrafluoro*-6-*nitrophenyl)mercury*. The crude compound (22% yield) was recrystallized from benzene, yield 18%, m.p. 201-202°.

The Reaction of Mercuric Trifluoroacetate with Trifluoromethanesulphonic Acid in Trifluoroacetic Acid

On addition of trifluoromethanesulphonic acid (10 mmol) to a solution of mercuric oxide (5 mmol) in trifluoroacetic acid (5 ml), mercuric trifluoromethanesulphonate was precipitated. It was collected and washed with petroleum spirit (b.p. 40-60°)/diethyl ether (1:1, v/v; dried over $MgSO_4$), yield, *ca.* 60%. Infrared absorption (4000-700 cm^{-1}): 3400m(vbr), 1620w(vbr), 1215vs(br), and 1190 and 1170sh, $\nu_{as}(SO_3)$ [11-13] and $\nu(CF_3)$ [13, 38d], 1029s and 1009s cm^{-1}, $\nu_s(SO_3)$ [11-13]. The compound formed yellow mercuric oxide when added to water.

The mercuric trifluoromethanesulphonate in hot ethanol (50 ml) was filtered into a solution of 2,2'-bipyridyl (25 mmol) in absolute ethanol. After evaporation of the solution to *ca.* 20 ml., *tris*(2,2'-*bipyridyl)-mercury*(II) *trifluoromethanesulphonate hydrate* crystallized. Recrystallization from water gave colourless crystals, which became opaque on drying (vacuum/silica gel), yield 30% (based on mercuric oxide), m.p. 202-203° (Found: C, 39.2; H, 2.5; Hg, 20.5; N, 8.3. $C_{32}H_{26}F_6HgN_6O_7S_2$ calcd.: C, 39.0; H, 2.7; Hg, 20.3; N, 8.5%). Infrared absorption: 3535 and 3490w(vbr), $\nu(OH)$ [44], 3090w, 3070w, 1649w, 1592s, 1579w, 1565w, 1490m, 1475s, 1440vs, 1317sh, 1281, 1270 and 1255vs, $\nu(SO_2)$ [11-13], 1220s, $\nu(CF_3)$ [13] , 1162vs, 1136s, $\nu(SO_2)$ [11-13] , 1096sh, 1077 and 1064w, 1026vs, $\nu(SO)$ [11-13] , 1010s, 971sh, 812w, 768vs, 755sh, 741sh, 734s, 649sh, 633vs, $\delta(SO_2)$ [13] , 571m, $\delta(SO_2)$ [13] , 515m, $\delta(CF_3)$ [13] , 496w, 410w cm^{-1}. Frequencies underlined are attributable [18] to 2,2'-bipyridyl. ^1H NMR spectrum [$(CD_3)_2CO$] : 7.74-7.88, m (2H, H5, 5'), 8.25-8.43, td (J 7.8, 1.7 Hz, 2H, H4, 4'), 8.64-8.84, m (4H, H3, 3', 6, 6'). ^{19}F NMR spectrum: 77.7, s (CF_3).

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