847. *The Preparation and Study of Some Pentafluorophenylmercury Compounds.*

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An introductory investigation of some pentafluorophenylmercury compounds is reported. Bispentafluorophenylmercury forms stable neutral co-ordination compounds with 2,2′-bipyridyl and 1,2-bis(diphenylphosphino)ethane. Cleavage of pentafluorophenylmercury compounds by hydrogen chloride, bromine, mercuric bromide, and dimethylmercury are described; different mechanisms appear to obtain for reactions with bromine and with hydrogen chloride. The electric polarisations of $(C_6F_5)_2Hg$, $C_6F_5{\cdot}HgMe$, $C_6F_5{\cdot}HgPh$, and $C_6F_5{\cdot}HgBr$ in benzene solution have been measured. It is assumed that bispentafluorophenylmercury is centrosymmetric and hence the apparent dipole moment is due to a high atom polarisation; dipole moments of pentafluorophenylmercury compounds are calculated on this basis.

DIFFERENCES between organometallic and metalloid compounds containing perfluoroalkyl groups and the corresponding alkyl compounds are often profound. Until the synthesis of bromopentafluoro- and pentafluoroiodo-benzene was achieved,[1] no route to the corresponding perfluoroaryl derivatives was available. Bromopentafluoro- and pentafluoroiodo-benzene form Grignard reagents easily and this makes possible the synthesis and investigation of pentafluorophenyl derivatives; Wall and his co-workers [2] have in fact prepared tetrakispentafluorophenylsilane, trispentafluorophenylphosphine, and trispentafluorophenylphosphine oxide from pentafluorophenylmagnesium bromide and the appropriate metalloid chloride. We report here the preparation of some pentafluorophenyl mercurials.

Pentafluorophenylmagnesium bromide reacts easily with mercuric chloride, give to bispentafluorophenylmercury. The thermal stability of this compound is significant; it was unchanged after 5 hours' heating at 250°. An increase in the thermal stability of aryl-mercurials with the introduction of electron-withdrawing substituents has been noted previously,[3] but the present observation shows that the migration of fluorine from a pentafluorophenyl group to mercury, leaving tetrafluorobenzyne, a process which could possibly be a source of instability, does not occur easily. In contrast to diaryl- and dialkyl-mercurials, which react easily with protonic acids and with halogens, bispentafluorophenylmercury is extremely resistant to protonic acids, *e.g.*, it recrystallises unchanged from concentrated sulphuric acid; the action of halogens is slow but equimolar quantities of bromine and bispentafluorophenylmercury in carbon tetrachloride are completely converted into pentafluorophenylmercuric bromide and pentafluorobromobenzene in 5 days at 60°.

Mixed alkylarylmercurials are usually thermally unstable and tend to disproportionate to symmetrical products.[3] No difficulty was experienced, however, in the preparation of methylpentafluorophenylmercury and this compound was unchanged when heated at 100° in an evacuated tube. Moreover, it can be formed by heating a mixture of dimethyl- and bispentafluorophenyl-mercury (see below). Pentafluorophenylphenylmercury showed no signs of decomposition at 200°.

The most remarkable feature of bispentafluorophenylmercury is its ability to form stable co-ordination compounds with donor molecules: complexes with bipyridyl and with 1,2-bis(diphenylphosphino)ethane have been isolated.[4] This is the first report that mercury

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[1] Nield, Stephens, and Tatlow, *J.*, 1959, 166.

[2] Wall, Donadio, and Pummer, *J. Amer. Chem. Soc.*, 1960, **82**, 4846.

[3] Kharasch and Grafflin, *J. Amer. Chem. Soc.*, 1925, **47**, 1948; Koton and Martynova, *Zhur. obshchei Khim.*, 1954, **24**, 2177; *Chem. Abs.*, 1956, **50**, 217.

[4] Dessy and Jin-Young Kim, *J. Amer. Chem. Soc.*, 1961, **83**, 1167, and references cited therein.

involved in a linkage to carbon, other than in cyanide, has sufficient electron-accepting capacity to enable neutral co-ordination complexes to be isolated. Neither methylpentafluorophenyl- nor pentafluorophenylphenyl-mercury formed analogous complexes. Bipyridyl forms no complexes with dimethyl-, diphenyl- or diphenylethynyl-mercury, though it forms an unstable complex with dimethylcadmium. Bistrifluoromethylmercury is surprisingly soluble in water and has a small but measurable conductivity in this solvent,[5] attributed to co-ordination of water to the mercury atom, followed by ionisation,[6] *i.e.*: $(CF_3)_2Hg \longrightarrow (CF_3)_2HgOH_2 \longrightarrow (CF_3)_2HgOH^- + H_3O^+$. Bispentafluorophenylmercury is insoluble in water but an M/8-solution could be prepared in 3 : 1 acetone–water at room temperature. No difference could be detected between the conductivity of this solution and that of the pure solvent, and therefore a process analogous to that (above) does not occur here, which is surprising in view of the stable co-ordination complexes just mentioned.

The electric polarisations of four pentafluorophenylmercury compounds in benzene solution have been measured, but the results are difficult to interpret. The symmetrical mercury diaryls belong to a group of compounds which display apparent permanent dipole moments in solution, though *X*-ray and other evidence indicates non-polarity. Compounds of this type which can be examined as gases have been shown to be non-polar, by the temperature-invariance of their total polarisation. The anomalous moments apparent from measurements of solutions have been ascribed to unusually large atom polarisations,[7] and this view has been strongly supported by recent calculations of atom polarisations from infrared frequencies.[8] Since atom polarisations are the sum of terms of the type, Constant × ν^{-2}, the bending modes of lowest frequency, least accessible to observation, make the biggest contributions. Very recently, the atom polarisation of *p*-benzoquinone was calculated from the infrared frequencies and intensities;[9] most of the anomalously large atom polarisation was accounted for, and 85% of the calculated (65—70% of the observed) atom polarisation was due to the vibration at 108 cm.$^{-1}$.

TABLE 1.

Dipole moments of some mercurials.

Compound	$_{T}P$	$_{E}P$ (R_D)	$_{A}P$	$_{O}P$	μ (D)
$(C_6F_5)_2Hg$	91	66	25	0	0
$MeHg{\cdot}C_6F_5$	211	45	12	154	2·8
$PhHg{\cdot}C_6F_5$	207	64	14	129	2·5
$C_6F_5{\cdot}HgBr$	69·5	44	12	13	(<1)

Diphenylmercury is centrosymmetric,[10] and the difference [11] between its total polarisation ($_{T}P$) and its electron polarisation (R_D) is 4 c.c. We feel justified in assuming that bispentafluorophenylmercury is also centrosymmetric, and we conclude that its atom polarisation is approximately $_{T}P - R_D = 25$ c.c. It is worth noting that the atom polarisation of silicon tetrafluoride, calculated from infrared intensities, is 4·4 c.c. (Whiffen [8]), so the value 25 c.c. for bispentafluorophenylmercury seems reasonable. In calculating orientation polarisation of the compounds $MeHg{\cdot}C_6F_5$, $PhHg{\cdot}C_6F_5$, and $C_6F_5{\cdot}HgBr$, we make an allowance of 2 c.c. for the atom polarisation of a PhHg group, and 12 c.c. for that of a $C_6F_5{\cdot}Hg$ group. This seems preferable to taking an arbitrary percentage of electron polarisation. Dipole moments calculated in this way are given in Table 1, in which $_{A}P$ represents atom polarisation, estimated as discussed above.

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[5] Emeléus and Haszeldine, *J.*, 1949, 2953.

[6] Lagowski, *Quart. Rev.*, 1959, **13**, 233.

[7] Smith and Angus, *Proc. Roy. Soc.*, 1932, *A*, **137**; Finn, Hampson, and Sutton, *J.*, 1938, 1254; Coop and Sutton, *J.*, 1938, 1269.

[8] Whiffen, *Trans. Faraday Soc.*, 1958, **54**, 327; Huang and Sullivan, *Nature*, 1960, **168**, 1104.

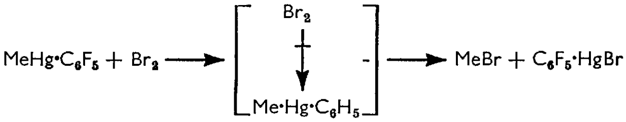
[9] Charney and Becker, *J. Amer. Chem. Soc.*, 1961, **83**, 4468.

[10] Kitaigorodski and Grdenic, *Izvest. Akad. Nauk S.S.S.R.*, 1948, **2**, 262.

[11] Hampson, *Trans. Faraday Soc.*, 1934, **30**, 877.

The bending frequency of mercury(II) bromide (vapour)[12] is only 41 cm.$^{-1}$, which suggests that the HgBr group has an appreciable atom polarisation. This would in turn further reduce the apparent dipole moment of pentafluorophenylmercuric bromide. The moments of the analogous compounds $\mathrm{MeHg{\cdot}C_6F_5}$ and $\mathrm{PhHg{\cdot}C_6F_5}$ are a little less than those of alkyl- and phenyl-mercury(II) bromides (3·1—3·5 D).[13]

Reaction of methylpentafluorophenylmercury with anhydrous hydrogen chloride resulted in the preferential cleavage of a pentafluorophenyl group as pentafluorobenzene, $\mathrm{MeHg{\cdot}C_6F_5} + \mathrm{HCl} \longrightarrow \mathrm{MeHgCl} + \mathrm{C_6HF_5}$, but a phenyl group was preferentially removed from pentafluorophenylphenylmercury, as benzene. Dessy and Jin-Young Kim[4] concluded, from a study of the cleavage of alkyl-aryl mercurials, that the rate of cleavage of a group from mercury, by hydrogen chloride, depends on the electron density at the mercury-bonded carbon atom. On this basis, the above results indicate that the electron density on the mercury-bonded carbon atom of a pentafluorophenyl group is reduced with respect to phenyl, but not to the extent that it is less than in methyl. Cleavage similar to that obtained with hydrogen chloride was expected to result from reaction with bromine; instead, a methyl group was removed preferentially, $\mathrm{MeHg{\cdot}C_6F_5} + \mathrm{Br_2} \longrightarrow \mathrm{MeBr} + \mathrm{C_6F_5{\cdot}HgBr}$, but phenyl and pentafluorophenyl groups were removed from pentafluorophenylphenylmercury in about equal amounts. It is apparent that different mechanisms must obtain for the reactions with bromine and hydrogen chloride. The ability of a pentafluorophenyl group to influence the acceptor properties of mercury to a considerable degree leads us to suggest that the reactions with bromine, mentioned above, pass through an intermediate complex where a bromine molecule is co-ordinatively bound to mercury, *i.e.*:



$$\mathrm{MeHg{\cdot}C_6F_5} + \mathrm{Br_2} \longrightarrow \left[\begin{array}{c}\mathrm{Br_2}\\ \downarrow\\ \mathrm{Me{\cdot}Hg{\cdot}C_6H_5}\end{array}\;-\right] \longrightarrow \mathrm{MeBr} + \mathrm{C_6F_5{\cdot}HgBr}$$

Factors influencing the decomposition of the intermediate would then be different from those which govern the simple electrophilic replacement by hydrogen chloride.

Although electrophilic attack on bispentafluorophenylmercury by protonic acids is extremely difficult, and reaction with halogens is much slower than in the case of diphenylmercury, reaction with mercury(II) bromide in methanol was very rapid, $\mathrm{(C_6F_5)_2Hg} + \mathrm{HgBr_2} \longrightarrow \mathrm{2C_6F_5{\cdot}HgBr}$. However, no reaction appeared to take place with mercury(II) iodide. A mixture of bispentafluorophenyl- and dimethyl-mercury rearranged within 12 hours at 60° to give methylpentafluorophenylmercury. When a bispentafluorophenylmercury that had been rigorously purified was used, reaction did not proceed very far, if at all, after 5 days at 100°. When a catalytic amount of pentafluorophenylmercuric bromide was added, exchange occurred and was complete after 12 hours at 60°. This indicates that the exchange $\mathrm{(C_6F_5)_2Hg} + \mathrm{Me_2Hg} \longrightarrow \mathrm{2C_6F_5{\cdot}HgMe}$, although very readily brought about, is entirely dependent on halide impurities as promoters.

This preliminary survey indicates that, in combination with mercury, the pentafluorophenyl group resembles a halogen atom rather than an aryl group.

EXPERIMENTAL

Bromopentafluorobenzene was obtained from the Imperial Smelting Corporation, and by bromination of pentafluorobenzene[1] which was prepared in this laboratory by chlorofluorination of benzene and dehalogenation of the product.[14] Fluorine analyses were carried out by Mr. T. Caygill, using the biphenyl–sodium method of decomposition.[15]

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[12] Klemperer and Lindeman, *J. Chem. Phys.*, 1956, **25**, 397.

[13] Wesson, " Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1949.

[14] Mobbs and Musgrave, *Chem. and Ind.*, 1961, 1268.

[15] Johncock, Musgrave, and Wiper, *Analyst*, 1959, **84**, 245.

Bispentafluorophenylmercury.—Pure, dry mercury(II) chloride (6·8 g., 25 mmoles) was extracted (Soxhlet) into a slight excess of pentafluorophenylmagnesium bromide [1] (51 mmoles) in ether (200 ml.) during 1 hr. Water (100 ml.) was added, the ether layer was separated and dried ($MgSO_4$), and then the ether was removed by vacuum-transfer. The solid residue was sublimed at 130°/10^{-3} mm., yielding white *bispentafluorophenylmercury* (9·8 g., 73%) which, recrystallised from carbon tetrachloride, had m. p. 142·3° (Found: F, 35·6; Hg, 38·0. $C_{12}F_{10}Hg$ requires F, 35·5; Hg, 37·6%), $\nu_{max.}$ 1639, 1504, 1481, 1471 (doublet), 1449sh, 1370, 1078sh, 1066, 1058 (doublet), 970, 961 (doublet), 806 cm.$^{-1}$ (sh = shoulder).

Bispentafluorophenylmercury (0·5 g.) was heated in an evacuated glass tube at 250° for 5 hr. Then the tube was opened to a vacuum-system, to remove any volatile material. No significant weight loss was observed and the remaining bispentafluorophenylmercury melted at 142°.

Bipyridyl (0·15 g., 1·0 mmole) in 1 : 1 v/v benzene–hexane was added to bispentafluorophenylmercury (1·0 mmole) in the same solvent. White needles of *bispentafluorophenyl-(bipyridyl)mercury* were slowly deposited (Found: F, 27·2; Hg, 28·4. $C_{22}H_6F_{10}HgN_2$ requires F, 27·5; Hg, 29·0%), having m. p. 122—123°, $\nu_{max.}$ 1504, 1466, 1431, 1361, 1072, 1053 (doublet), 962 and 746 cm.$^{-1}$. Weak absorption was present at 1634 cm.$^{-1}$, in the region where all the pentafluorophenyl derivatives so far examined absorb.

An analogous method slowly afforded white *bispentafluorophenyl-*1,2-*bis*(*diphenylphosphino*)-*ethanemercury*, m. p. 158—159° (Found: F, 21·1; Hg, 20·6. $C_{38}H_{24}F_{10}HgP_2$ requires F, 20·4; Hg, 21·5%), $\nu_{max.}$ 1504, 1468, 1453sh, 1445sh, 1429, 1368, 1075, 1064 (doublet), 962, 730, and 692 cm.$^{-1}$ (weak absorption at 1637 cm.$^{-1}$).

Pentafluorophenylmercury(II) *Bromide.*—Bispentafluorophenylmercury (0·80 g., 1·5 mmoles) and mercury(II) bromide (0·54 g., 1·5 mmoles) were heated in methanol (15 ml.) for 4 hr. Removal of the solvent by vacuum-transfer left *pentafluorophenylmercury*(II) *bromide* which, when recrystallised from carbon tetrachloride, had m. p. 155° (Found: C, 15·5; Br, 18·6; F, 20·6. C_6BrF_5Hg requires C, 16·0; Br, 17·9; F, 21·2%), $\nu_{max.}$ 1637, 1515, 1481sh, 1471, 1453sh, 1093, 970sh, and 961 cm.$^{-1}$.

Methylpentafluorophenylmercury.—Methylmercury(II) iodide (12 g., 35 mmoles) was added as a suspension in ether to pentafluorophenylmagnesium bromide (50 mmoles) in ether. The mixture was heated under reflux for 4 hr., then worked up (cf. above), yielding *methylpentafluorophenylmercury* (9·2 g., 69%), which when sublimed in a vacuum and recrystallised from ethanol–water had m. p. 36° (Found: F, 24·2. $C_7H_3F_5Hg$ requires F, 24·8%), $\nu_{max.}$ 1642, 1513, 1466, 1370, 1267, 1079, 1066, 1058 (triplet), 958, 794, and 781 cm.$^{-1}$.

Pentafluorophenylphenylmercury.—A suspension of phenylmercury(II) chloride (12 g., 38 mmoles) in ether was added to pentafluorophenylmagnesium bromide (50 mmoles) in ether. The mixture was heated under reflux for 12 hr., then worked up as described above. *Pentafluorophenylphenylmercury* was purified by vacuum-sublimation (6·9 g., 40%) (Found: C, 32·9; F, 20·8. $C_{12}H_5F_5Hg$ requires C, 32·4; F, 21·4%) and then had m. p. 164°, $\nu_{max.}$ 1645, 1513, 1471, 1449sh, 1437sh, 1374, 1269, 1087sh, 1080, 1065, 1053, 1029, 1015, 1000, 962, 794, 735, 719, and 699 cm.$^{-1}$.

Cleavage.—(*a*) *With hydrogen chloride.* (i) Methylpentafluorophenylmercury (0·80 g., 2·1 mmoles) was weighed into a small tube and then hydrogen chloride (0·085 g., 2·1 mmoles) was condensed into the tube from a vacuum-system. The tube was sealed under a vacuum and was then immersed in a bath at −78° which was allowed gradually to reach room temperature. The tube was opened to a vacuum-system; the volatile material removed was identified as pentafluorobenzene (0·34 g., 2·02 mmoles) by its infrared spectrum. The remaining solid was pure methylmercury(II) chloride (0·53 g., 2·1 mmoles), m. p. 171° (lit., 170°), whose infrared spectrum confirmed the absence of pentafluorophenylmercury(II) chloride.

(ii) Pentafluorophenylphenylmercury (0·617 g., 1·4 mmoles) and hydrogen chloride (0·051 g., 1·4 mmoles) were allowed to react as above. The volatile material was identified by its infrared spectrum as benzene (0·10 g., 1·3 mmoles) containing a trace of pentafluorobenzene; the remaining solid was *pentafluorophenylmercury*(II) *chloride* (0·54 g., 1·3 mmoles) (Found: F, 22·9. C_6ClF_5Hg requires F, 23·6%), m. p. 165°, $\nu_{max.}$ 1639, 1515, 1471, 1451sh, 1379, 1370 (doublet), 1092, 1073, 1063, and 813 cm.$^{-1}$.

(*b*) *With bromine.* (i) Methylpentafluorophenylmercury (1·04 g., 2·7 mmoles) was dissolved in dry decane (20 ml.) contained in an evacuated two-necked flask, fitted with a small dropping-funnel and a tap for attachment to a vacuum-system. The flask was cooled in ice, and bromine (0·43 g., 2·7 mmoles) in decane (5 ml.) was slowly admitted with shaking. The mixture was not as quickly decolorised as in the reaction with pentafluorophenylphenylmercury (see below), so it was set aside overnight. Some volatile material was then transferred under vacuum from the decane to a vacuum-system. After several fractionations *in vacuo*, through a cooling-bath containing solid carbon tetrachloride, methyl bromide (0·10 g.) was obtained that was identified by its infrared spectrum. The remaining decane solution was cooled and a solid was filtered off that was shown to be pentafluorophenylmercury(II) bromide (1·01 g., 2·3 mmoles) by its infrared spectrum.

(ii) By the technique described above, bromine (0·35 g., 2·2 mmoles) in dry decane (5 ml.) was added very slowly to a cooled solution of pentafluorophenylphenylmercury (0·98 g., 2·2 mmoles) in decane (20 ml.). The bromine reacted quickly, and a white precipitate was formed; this was filtered off. It (0·65 g.) melted over a range, and the infrared spectrum indicated approximately equal quantities of phenylmercury(II) bromide and pentafluorophenylmercury(II) bromide.

(*c*) *With dimethylmercury.* Bispentafluorophenylmercury (0·5 g.) and an exess of dimethylmercury, contained in an evacuated Carius tube, were warmed to 60°. The solid dissolved but crystallised again on cooling. After the mixture had been at 60° for 12 hr., no solid crystallised on cooling; the tube was opened and the excess of dimethylmercury was removed by vacuum-transfer. The remaining solid, m. p. 34°, gave the infrared spectrum of methylpentafluorophenylmercury. When this reaction was repeated, but with bispentafluorophenylmercury that had been recrystallised four times from carbon tetrachloride (to remove any halide impurities), the bispentafluorophenylmercury was very little affected in 12 days at 100°. This bispentafluorophenylmercury was then mixed with pentafluorophenylmercury(II) bromide (0·01 g.) and then warmed to 60° with dimethylmercury, as described above; it was then converted completely into methylpentafluorophenylmercury within 12 hr.

TABLE 2.

10^3w	$\Delta\varepsilon/w$	$10^2\Delta n/w$	$-\Delta v/w$
	$MeHg{\cdot}C_6F_5$		
4·620	16·667	—	—
12·058	16·248	—	0·731
14·487	16·113	0·500	—
17·833	16·128	—	0·734
10·241	—	0·442	—
14·249	—	—	0·739
	$PhHg{\cdot}C_6F_5$		
3·682	11·678	1·475	0·682
7·126	—	1·525	0·699
9·061	11·919	—	0·691
13·371	12·191	—	—
16·360	—	2·104	—
	$C_6F_5{\cdot}HgBr$		
3·546	—	3·065	0·877
6·520	2·607	2·500	0·857
11·839	2·449	—	0·869
15·951	2·508	2·215	—
	$(C_6F_5)_2Hg$		
3·473	—	—	0·749
7·133	2·102	1·524	0·782
10·995	2·002	1·318	0·753
14·521	1·860	1·497	0·751

Measurements of Dipole Moments.—Results are given in Table 2, where the usual notations apply, refractive indices (n), specific volumes (v), weight fractions of the solute (w); $\Delta\varepsilon = \varepsilon_S - \varepsilon_B$, where ε_S = dielectric constant of the solution and ε_B = dielectric constant of benzene, and similarly for Δn and Δv. The measurements refer to benzene solution at 25°.

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