Pentafluorophenylarsenic Compounds [1]

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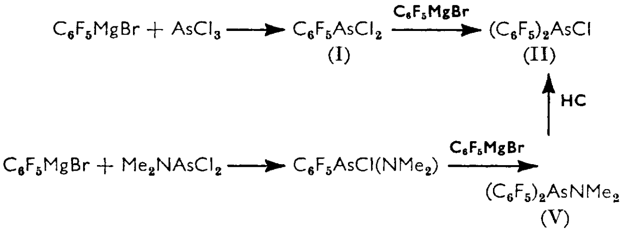
The preparation of pentafluorophenylarsonous dichloride and bispentafluorophenylarsinous chloride is described. Their neutral hydrolysis affords $(C_6F_5AsO)_n$ and $[(C_6F_5)_2As]_2O$ respectively, whereas alkaline hydrolysis produces pentafluorobenzene quantitatively. Silver sulphide reacts with them to give $(C_6F_5AsS)_4$ and $[(C_6F_5)_2As]_2S$ respectively, from which the respective chlorides are re-formed on treatment with mercuric chloride. Mercuration of $(C_6F_5)_2AsCl$ and $[(C_6F_5)_2As]_2S$ affords separable isomeric mixtures of $[(C_6F_5)_2As]_2$. Similar mixtures are obtained from $(C_6F_5)_2AsCl$ and PH_3 or $(CH_3)_3SiH$. Mercuration of $C_6F_5AsCl_2$ gives the four-membered arsenic ring compound $(C_6F_5As)_4$.

TRISPENTAFLUOROPHENYLARSINE [2] is obtained by the reaction of arsenic trichloride with pentafluorophenylmagnesium bromide. Reaction of methylpentafluorophenylmercury with arsenic tribromide affords pentafluorophenylarsonous dibromide.[3] Aside from these observations little is known about the chemistry of pentafluorophenylarsenic derivatives.

Pentafluorophenylarsonous dichloride (I) is conveniently prepared by the reaction of pentafluorophenylmagnesium bromide with a four-fold excess of arsenic trichloride. The use of lower molar proportions of arsenic trichloride results in the formation of bispentafluorophenylarsinous chloride (II), which is, however, best prepared by the reaction of dimethylaminoarsinous dichloride with pentafluorophenylmagnesium bromide followed by cleavage of the arsenic–nitrogen bond in the amide (V) with anhydrous hydrogen chloride. These reactions are summarised in Scheme 1.

It is evident that nucleophilic attack by the Grignard reagent on the fluoroaromatic ring does not occur, and that the arsenic–chlorine bond in the intermediate *NN*-dimethylpentafluorophenylarsonamidous chloride is selectively attacked by C_6H_5MgBr.



SCHEME 1

Pentafluorophenylarsonous dichloride reacts rapidly

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[1] For a preliminary account, see M. Green and D. Kirkpatrick, *Chem. Comm.*, 1967, 57.

[2] M. Fild, O. Glemser, and G. Christoph, *Angew. Chem.*, 1964, **3**, 801.

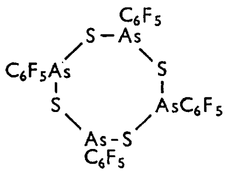
[3] R. D. Chambers and J. Cunningham, *Tetrahedron Letters*, 1965, 2389.

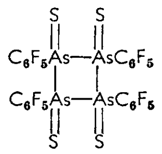
with water to afford poly(pentafluorophenylarsoxane) (III), $[C_6F_5AsO]_n$, a stable high-melting solid. Its insolubility limited molecular-weight measurements, and attempts to obtain an arsoxane of lower molecular weight by variation of the hydrolysis conditions were unsuccessful.

Bispentafluorophenylarsinous chloride also reacts with water to give stable crystalline tetrakispentafluorophenyldiarsoxane (IV), $(C_6F_5)_2AsOAs(C_6F_5)_2$, which sublimed *in vacuo*. The pentafluorophenylphosphorus chlorides afford phosphorus acids on hydrolysis.[4] The formation of arsenic oxides rather than the corresponding arsenic acids on hydrolysis of (I) and (II) may be ascribed[5] to the weaker dp_{π} bonding between As_{4d}–O_{2p} orbitals than the stronger P_{3d}–O_{2p} interaction, which facilitates the condensation reaction $2As{-}OH \longrightarrow As{-}O{-}As + H_2O$.

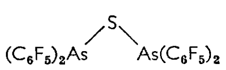
Pentafluorobenzene is produced quantitatively on treatment of pentafluorophenylarsonous dichloride and bispentafluorophenylarsinous chloride with aqueous sodium hydroxide. These reactions probably proceed *via* nucleophilic attack on the arsenic atom with displacement of $C_6F_5^-$, which captures a proton from the solvent.

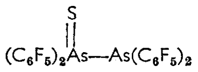
The dichloride (I) slowly reacts with a suspension of silver sulphide in benzene to give a stable crystalline thioarsine (VI). Molecular-weight measurements in solution suggest the presence of an eight-membered ring. Reaction of (VI) with mercuric chloride in ether results in cleavage of the (AsSAs) system to form $C_6F_5AsCl_2$, an observation which is more consistent with the structure (VI) than alternative formulations such as (VII), which involves pentaco-ordinate arsenic atoms. The low solubility of (VI) precluded detailed ^{19}F n.m.r. studies.


(VI)

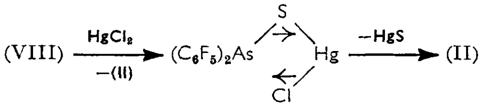

(VII)

Bispentafluorophenylarsinous chloride reacts with silver sulphide in benzene to afford a crystalline solid, which can be sublimed *in vacuo*, and is formulated as the thiodiarsine (VIII). The ^{19}F n.m.r. spectrum of (VIII) shows only three peaks of the expected multiplicity, and since the chemical shifts of the *ortho*, *meta*, and *para* fluorines are sensitive to the nature of the groups attached to the arsenic, unsymmetrical structures such as (IX) can be excluded.


(VIII)


$(C_6F_5)_2As(=S){-}As(C_6F_5)_2$
(IX)

Bispentafluorophenylarsinous chloride is obtained by the reaction of the thiodiarsine (VIII) with mercuric chloride; the reaction probably proceeds as in Scheme 2.



SCHEME 2

The reaction of (VIII) with mercury proceeds smoothly to give tetrakis(pentafluorophenyl)diarsine (X), a stable crystalline solid. The diarsine is also obtained by reaction of (II) with mercury, phosphine, or trimethylsilane. The reactions with PH_3 or Me_3SiH were expected to provide a route to the unknown $(C_6F_5)_2AsH$, but the arsine probably reacts immediately with unchanged $(C_6F_5)_2AsCl$ to give the diarsine.

After recrystallisation from benzene the diarsine was characterised by elemental analyses and molecular-weight measurements in chloroform. However, the analytical sample melted over a wide range, and examination of the ^{19}F n.m.r. spectrum showed the presence of five peaks, clearly inconsistent with the molecular formula $[(C_6F_5)_2As]_2$. Sublimation of the diarsine *in vacuo* allowed the separation of two isomers (Xa) and (Xb) of tetrakis(pentaphenyl)diarsine (X). The ^{19}F n.m.r. spectrum (Table 1) of each isomer showed three peaks in the ratio of 2 : 1 : 2 with the expected multiplicity. Prolonged heating of isomer (Xb) *in vacuo* resulted in some decomposition, but also gave a mixture of the two isomers (Xa) and (Xb).

We suggest that the two isomers are rotamers, possibly *trans* and *gauche* forms of $(C_6F_5)_2AsAs(C_6F_5)_2$. The corresponding diphosphine $(C_6F_5)_2PP(C_6F_5)_2$, the preparation of which has recently been reported,[8] was also prepared. The ^{19}F n.m.r. spectrum of the diphosphine showed only three peaks corresponding to the presence of only one isomer.

The implied high energy barrier for the interconversion of the two diarsine isomers can be attributed to steric hindrance by the *ortho* fluorines, and the As–As bond length, which is such that the *gauche* form can be formed but is not long enough to allow free rotation. The shorter P–P bond length probably results in the locking of the diphosphine $(C_6F_5)_2PP(C_6F_5)_2$ in the more stable *trans* conformation.

Mercury reacts with pentafluorophenylarsonous dichloride to produce tetrakispentafluorophenylcyclotetra-arsine $(C_6F_5As)_4$ (XI), a benzene-soluble compound, which was characterised by elemental analyses and molecular-weight measurements in solution and by mass spectrometry. The ^{19}F n.m.r. spectrum (Table 1) supports the molecular formula $(C_6F_5As)_4$. It is noteworthy that the only previously reported[6] As_4 ring compound is $(CF_3As)_4$. The corresponding methylarsenic and phenyl-

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[4] D. D. Magnelli, G. Tesi, J. U. Lowe, jun., and W. E. McQuistion, *Inorg. Chem.*, 1966, **5**, 457; M. Green, R. N. Haszeldine, and H. G. Higson, unpublished observations.

[5] A. B. Burg and J. W. Singh, *J. Amer. Chem. Soc.*, 1965, **87**, 1213.

[6] A. H. Cowley, A. B. Burg, and W. R. Cullen, *J. Amer. Chem. Soc.*, 1966, **88**, 3128.

arsenic homocyclic compounds have five- and six-membered ring structures, respectively.[7] We suggest that the four-membered arsenic ring compound $(C_6F_5As)_4$ has a puckered structure.

The diarsines (Xa) and (Xb) both react slowly with an excess of chlorine at room temperature to give arsenic trichloride and chloropentafluorobenzene, which implies that the arsorane $(C_6F_5)_2AsCl_3$ readily disproportionates. This contrasts with the reported[8] stability of $(C_6F_5)_2PCl_3$.

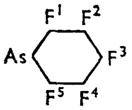
EXPERIMENTAL

For analyses, see Table 2.

Pentafluorophenylarsonous Dichloride (I).—Pentafluorophenylmagnesium bromide [from bromopentafluorobenzene (49·4 g., 0·20 mole) and magnesium (0·6 g., 0·25 mole) in ether (250 ml.)] was added very slowly dropwise to a stirred refluxing solution of arsenic trichloride (147·3 g., 0·811 mole) in ether (100 ml.). The mixture was refluxed for 2 hr., and filtered, and the solvent removed *in vacuo*. Distillation of the residue gave the *dichloride* (I) (41·7 g., 1·33 mole, 66%) as a colourless liquid, b. p. 52°/0·1 mm., $\nu_{max.}$ (liquid film) 1639m, 1514s, 1482s, 1381m, 1288m, 1146w, 1085s, 1030vw, 1012w, 977s, 809w, 751vw, and 723w cm.$^{-1}$.

TABLE 1

Fluorine-19 chemical shifts (p.p.m.) *



Compound	$\delta_{(1)}(=\delta_{(5)})$	$\delta_{(2)}(=\delta_{(4)})$	$\delta_{(3)}$	$J_{1,3}(=J_{3,5})$	$J_{2,3}(=J_{3,4})$	$J_{1,2}(=J_{5,4})$
$C_6F_5AsCl_2$ (I)	130·1	159·8	146·3	$\lvert 6·0 \rvert$	±21·1	±21·0
$(C_6F_5)_2AsCl$ (II)	128·6	159·8	148·5	$\lvert 5·0 \rvert$	±21·0	±22·2
$[(C_6F_5)_2As]_2O$ (III)	133·5	162·8	151·8	$\lvert 5·0 \rvert$	±21·1	±20·3
$(C_6F_5AsS)_4$ (VI)	127·4	162·4	151·2	—	—	—
$[(C_6F_5)_2As]_2S$ (VIII)	129·2	163·2	150·9	$\lvert 6·1 \rvert$	±21·0	±22·0
$(C_6F_5As)_4$ (XI)	125·9	161·8	152·1	$\lvert 5·0 \rvert$	±21·0	±21·8
$[(C_6F_5)_2As]_2$ (Xa)	133·3	162·8	152·0	$\sim\lvert 5·0 \rvert$	±23·0	±23·1
$[(C_6F_5)_2As]_2$ (Xb)	133·8	160	146·6	$\sim\lvert 5·0 \rvert$	±20·5	±20·0

* Studied in chloroform soln.; chemical shifts (±0·1 p.p.m.) are relative to CCl_3F increasing to high field.

TABLE 2

Pentafluorophenylarsenic compounds

	Found						Required					
	C	F	Cl	As	S	*M**	C	F	Cl	As	S	*M*
(I)	22·8	30·3	22·5	23·8	—	327	23·0	30·4	22·7	24·0	—	313
(II)	32·2	42·8	8·0	17·1	—	431	32·4	42·8	8·0	16·9	—	444
(III)	27·9	36·8	—	27·8	—	—	27·9	36·8	—	29·1	—	—
(IV)	34·5	45·4	—	17·8	—	834†	34·5	45·6	—	18·0	—	834
(VI)	26·2	34·9	—	27·2	11·6	1033	26·3	34·7	—	27·4	11·7	1096
(VIII)	34·0	42·1	—	17·6	3·7	802	33·9	44·7	—	17·7	3·8	850
(Xa)	35·0	46·4	—	18·2	—	755	35·2	46·5	—	18·3	—	818
(Xb)	35·2	46·6	—	18·4	—	770	35·2	46·5	—	18·3	—	818
(XI)	29·9	39·1	—	30·9	—	941 968†	29·8	39·3	—	31·0	—	968

* Determined in chloroform with a Mechrolab vapour-pressure osmometer. † Mass spectroscopy.

Bispentafluorophenylarsinous Chloride (II).—Pentafluorophenylmagnesium bromide [from bromopentafluorobenzene (49·4 g., 0·20 mole) and magnesium (6·0 g., 0·25 mole) in ether (100 ml.)] was added dropwise to a stirred solution of dimethylaminoarsonous dichloride (19·0 g., 0·10 mole) in ether (100 ml.) at room temperature. The solution was refluxed for 2 hr., and filtered, and the filtrate saturated with dry hydrogen chloride. The ether was removed *in vacuo*, and the product extracted with pentane. Evaporation of the pentane followed by distillation of the residue gave the *chloride* (II) (34·3 g., 0·077 mole, 77%) as a colourless liquid, b. p. 82°/0·1 mm., $\nu_{max.}$ (liquid film) 1639m, 1514s, 1480s, 1380m, 1286m, 1144w, 1083s, 1032vw, 1012w, 974s, 804w, 758vw, and 723vw cm.$^{-1}$.

Hydrolysis of Pentafluorophenylarsonous Dichloride.—The dichloride (1·60 g., 5·11 mmoles) was shaken under nitrogen with 'boiled-out' distilled water (5 ml.) at room temperature. The white solid was filtered off and washed with water to give, after drying *in vacuo*, *poly(pentafluorophenylarsoxane)* (III) (1·04 g., 79% per C_6F_5As), m. p. *ca.* 217° (decomp.), $\nu_{max.}$ (Nujol and hexachlorobutadiene) 2920vw, 2646w, 2590w, 2560w, 2420w, 2340w, 1941vw, 1917vw, 1868vw, 1722w, 1640m, 1615w, 1585w, 1555s, 1472s, 1459w, 1372m, 1295m, 1237vw, 1133vw, 1104m, 1090s, 1033w, 1015w, 969s, 806w, 780vw, 778s, 723w, 662s, and 651s cm.$^{-1}$.

Hydrolysis of Bispentafluorophenylarsinous Chloride.—The dichloride (1·49 g., 3·34 mmoles) was shaken with water

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[7] J. H. Burns and J. Waser, *J. Amer. Chem. Soc.*, 1957, **79**, 859; K. Hedberg, E. W. Hughes, and J. Waser, *Acta Cryst.*, 1961, **14**, 369; S. E. Rasinnssen and J. Danielson, *Acta Chem. Scand.*, 1960, **14**, 1862.

[8] H. G. Ang and J. M. Miller, *Chem. and Ind.*, 1966, 945.

(5 ml.) at room temperature. The white precipitate was filtered off, dried *in vacuo*, recrystallised from pentane, and sublimed to give *tetrakispentafluorophenyldiarsoxane* (IV) (1·32 g., 1·58 moles, 94·4%), m. p. 108—108·5°, $\nu_{\text{max.}}$ (Nujol and hexachlorobutadiene) 2919vw, 2892vw, 2750vw, 2649w, 2558w, 2520vw, 2418w, 2350w, 2222vw, 1947w, 1867w, 1773vw, 1725w, 1639m, 1618vw, 1582w, 1512s, 1478s, 1377m, 1280m, 1243vw, 1142m, 1080s, 1048w, 1020m, 1009m, 970s, 808m, 760m, 738m, 723m, and 657vw cm.$^{-1}$.

Reaction of Pentafluorophenylarsonous Dichloride with Alkali.—The dichloride (4·0 g., 12·67 mmoles) was treated at 70° with aqueous sodium hydroxide (20 ml. of a 20% solution) for 2 hr. After cooling, an immiscible liquid separated and was identified (infrared) as pentafluorobenzene (2·1 g., 12·4 mmoles, 97·5%).

Reaction of Bispentafluorophenylarsinous Chloride with Alkali.—The chloride (4·1g., 9·14 mmoles) was similarly treated with aqueous sodium hydroxide (20 ml. of a 20% solution) to give pentafluorobenzene (2·90 g., 17·3 mmoles, 94·3%).

Reaction of Pentafluorophenylarsonous Dichloride with Silver Sulphide.—The dichloride (3·73 g., 11·9 mmoles) and a suspension of silver sulphide (5·0 g., 20 mmoles) in dry benzene (30 ml.) were refluxed in a nitrogen atmosphere for 48 hr. Silver chloride was filtered off and the solvent removed *in vacuo* from the filtrate. Unchanged (I) was removed by extraction with pentane. The residue was recrystallised from benzene to give *tetrakispentafluorophenylcyclotetra-arsonous tetrasulphide* (VI) (1·02 g., 0·93 mmole, 32%), m. p. 169—169·5°, $\nu_{\text{max.}}$ (Nujol and hexachlorobutadiene) 2918w, 2848w, 2646vw, 2557vw, 2418vw, 2342vw, 1639m, 1516s, 1475vs, 1376s, 1338vw, 1287m, 1136w, 1090m, 1028vw, 1011w, 970s, 803m, 750w, 722m, and 680w cm.$^{-1}$.

Reactions of Bispentafluorophenylarsinous Chloride with Silver Sulphide.—The chloride (2·7 g., 6·1 mmole) and silver sulphide (5·0 g., 20 mmole) in dry benzene (35 ml.) similarly gave a white solid, which after recrystallisation from benzene–pentane followed by sublimation gave *tetrakispentafluorophenyldiarsinous sulphide* (VIII) (2·21 g., 2·60 mmoles, 86%), m. p. 85—85·5°, $\nu_{\text{max.}}$ (Nujol and hexachlorobutadiene) 2918w, 2854vw, 2650w, 2590w, 2560w, 2420w, 2349w, 2222vw, 2062vw, 1942w, 1878w, 1724w, 1640m, 1615vw, 1584vw, 1516s, 1477vw, 1381s, 1347w, 1339w, 1286m, 1243w, 1139m, 1092s, 1042w, 1019m, 974s, 806m, 756w, and 725m cm.$^{-1}$.

Reaction of Tetrakispentafluorophenylcycloarsonous Tetrasulphide with Mercuric Chloride.—A solution of (VI) (1·20 g., 1·10 mmoles) and mercuric chloride (2·50 g., 9·20 mmoles) in dry ether (30 ml.) was refluxed under nitrogen for ½ hr. The precipitate was filtered off and the residue distilled *in vacuo* to give pentafluorophenylarsonous dichloride (1·22 g., 3·9 mmoles, 88·6%), identical (infrared) with an authentic sample.

Reaction of Tetrakispentafluorophenyldiarsinous Sulphide with Mercuric Chloride.—A solution of (VIII) (3·66 g., 4·31 mmoles) and mercuric chloride (2·50 g., 9·20 mmoles) in dry ether (30 ml.) was refluxed under nitrogen for ½ hr. The pale yellow precipitate was filtered off and the residue distilled *in vacuo* to give bispentafluorophenylarsinous chloride (3·67 g., 8·25 mmoles, 96%), identical (infrared) with an authentic sample.

Reaction of Tetrakispentafluorophenyldiarsinous Sulphide with Mercury.—A solution of (VIII) (3·06 g., 3·60 mmoles) in dry benzene (20 ml.) was added to mercury (70 g.) and refluxed under nitrogen with stirring for 12 hr. The black mixture was filtered. Evaporation of the solvent followed by recrystallisation of the residue from benzene gave a mixture of the two isomers of tetrakispentafluorophenyldiarsine (2·0 g., 2·44 mmoles, 68%) identified by infrared and ^{19}F n.m.r. spectroscopy.

Reaction of Bispentafluorophenylarsinous Chloride with Mercury.—The chloride (II) (2·5 g., 5·62 mmoles) was shaken vigorously with mercury (60 g., 0·30 mole) at 70° for 1 hr. The mixture was extracted with hot benzene (50 ml.). Evaporation of the solvent *in vacuo* followed by recrystallisation of the residue from benzene–pentane gave a mixture of the two *isomers* of tetrakispentafluorophenyldiarsine (2·2 g., 2·7 mmoles, 91%). The ^{19}F n.m.r. spectrum showed bands at 133·5, 146·6, 152·0, 160·0, and 162·8 p.p.m. Fractional sublimation *in vacuo* of the above material gave material subliming at 130—160° (Xa) (*ca.* 80%) with $\nu_{\text{max.}}$ (Nujol and hexachlorobutadiene) 1640m, 1510s, 1478s, 1381m, 1284m, 1262vw, 1148w, 1142w, 1080s, 1020w, 1010w, 974s, 935vw, 806m, 761m, 738m, and 725m cm.$^{-1}$. the fraction subliming at 220—240° (Xb) (*ca.* 20%) had $\nu_{\text{max.}}$ (Nujol and hexachlorobutadiene) 1640m, 1514m, 1490s, 1393m, 1378w, 1345vw, 1294m, 1157w, 1093s, 1016vw, 982s, 935m, 879w, 793m, 758w, and 726m cm.$^{-1}$.

Reaction of Pentafluorophenylarsinous Dichloride with Mercury.—The dichloride (I) (3·36 g., 10·7 mmoles) was shaken vigorously with mercury (60 g., 0·30 mole), the mixture being slowly warmed to 100° during 3 hr. The mixture was extracted with hot benzene (50 ml.). Evaporation of the solvent followed by recrystallisation from benzene–pentane gave *tetrakispentafluorophenylcyclotetra-arsine* (XI) (1·92 g., 1·98 mmoles, 74%), m. p. 141°, $\nu_{\text{max.}}$ (Nujol and hexachlorobutadiene) 2642vw, 2558vw, 2413vw, 2340vw, 1720vw, 1638m, 1613w, 1580w, 1549w, 1510s, 1474s, 1458w, 1374m, 1282m, 1143m, 1140m, 1087w, 1074s, 1068s, 1010w, 968s, 804m, 723w, and 675vw cm.$^{-1}$.

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