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SHORT COMMUNICATION

The Reaction of 1,2-Dilithiotetrafluorobenzene with Group V Halides.

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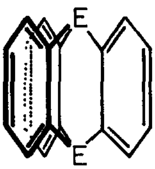
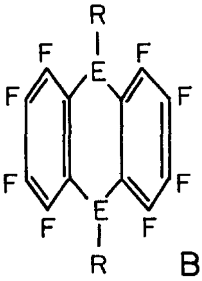
Although the arsenic containing analogue of triptycene, 5,10-*o*-benzenoarsanthrene *A* (E=As) was isolated some time ago [1] the related derivatives of antimony and bismuth are unknown. We now find that when 1,2-diiodotetrafluorobenzene is treated with methyllithium at -78°, to afford the little studied dilithiotetrafluorobenzene [2], and the appropriate metal chloride is added to the resulting solution, perfluorinated analogues of *A* (E = As, Sb, or Bi) are obtained in good yield. These are stable volatile solids.



A

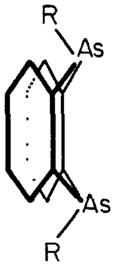


B

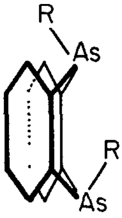
Derivatives of the type *B*, R = halogen, are not obtained if an excess of metal trichloride is used. Phosphorus trihalides do not afford similar products.

Reaction of the same dilithio compound with dichlorophenylphosphine, diiodomethylarsine, or diiodophenylarsine gives the anticipated dihydroarsanthrene and phosphanthrene derivatives B (E = As, R = CH_3; E = As, R = C_6H_5; E = P, R = C_6H_5) in moderate yield.

Chatt and Mann [3] isolated two forms of 5,10-dihydro-5,10-di-*p*-tolylarsanthrene which were assigned the *cis* and *trans* structures C and D, R = *p* -tolyl, on the basis of conformational deductions.



C



D

Similar arguments led Mann to suggest that the angle between the phenylene rings of the dimethylarsanthrene derivatives C and D (R = CH_3) would be ~121° [4]. A subsequent solid state study [5] showed that the angle was 117° but that only the *cis* form was present. Two forms of 5,10-dihydro-5,10-diethylphosphanthrene have also been assigned similar "butterfly" structures [1,5].

In marked contrast, the solid state structure [6] of 5,10-dihydro-5,10-dimethyloctafluoroarsanthrene is such that the molecule is almost flat and has a centre of inversion so that the methly groups are *trans* to each other. Only one isomer is present as is expected from the ^1H n.m.r. spectrum although the rings could be flexing in solution without inversion at the arsenic atoms [7].
The structure of 10-chlorophenoxarsine, its antimony pentachloride-oxide adduct and 10-phenoxarsine sulphide show dihedral angles between the aromatic rings of 156°, 167°, and 176.6° (average) [8-10]. The

corresponding angle in 10-chloro-5,10-dihydrophenarsazine is 169° [11]. All these results probably reflect the effect of crystal packing forces on the presumably low barrier to ring flexing in these "butterfly" molecules [7].

Experimental

All operations were carried out in dry apparatus using an atmosphere of dry oxygen-free nitrogen. A typical reaction is described below and other details are given in Table 1.

Preparation of 5,10-dihydro-5,10-dimethyloctafluoroarsanthrene.

Into a 500 ml three-necked round bottom flask fitted with stirrer, nitrogen inlet, dropping funnel, condenser, drying tube and septum was placed 4.02 g (10 mmoles) of 1,2-diiodotetrafluorobenzene in 250 ml anhydrous diethyl ether. The reaction vessel was flushed with nitrogen, cooled to -78°, and 12 ml of 1.7 M methyllithium was added dropwise with a syringe over a period of 10 minutes. The mixture was left to stir at -78° for 30 min. Diiodomethylarsine (3.44 g, 10 mmoles) in 100 ml THF was added dropwise, and after another 3 h the mixture was allowed to warm up to room temperature. The reaction mixture was filtered and the filtrate evaporated to dryness. The oily residue was dissolved in dichloromethane and chromatographed on Florisil using dichloromethane as solvent. This gave a white solid residue. Fractional recrystallization of the solid from hexane yielded two products, the first crop was a small amount of a white solid which is probably di-(*o*-iodotetrafluorophenyl)methylarsine (0.2 g, 7%), m.p. 175° ^{1}H n.m.r.; 1.55 p.p.m. singlet. ^{19}F n.m.r.; 126.8, 128.4, 156.0 p.p.m. multiplets of area ratio 1:1:2. The second white crystalline solid was

TABLE 1

Physical properties of new compounds*

					Anal.			
					C		H	
	% Yield	m.p.(°C)	^1H n.m.r.	^{19}F n.m.r.	Calcd.	Found	Calcd.	Found
$(CH_3As)_2(C_6F_4)_2$	62	105	1.58	123.6 153.6	35.3	35.2	1.26	1.26
$(C_6H_5As)_2(C_6F_4)_2$	51	118	7.22	122.2 153.0	48.0	47.4	1.67	1.66
$(C_6H_5P)_2(C_6F_4)_2$	35	89	7.52	122.0 152.8	56.3	56.2	1.95	1.90
$As_2(C_6F_4)_3$	70	200		122.4 153.0	36.4	36.1		
$Sb_2(C_6F_4)_3$	61	155		112.8 150.0	31.4	31.3		
$Bi_2(C_6F_4)_3$	65	>300°(dec)		109.4 154.0	25.1	25.0		

*N.m.r. spectra were run using a Varian T 60 instrument. ^1H spectra are given in p.p.m. downfield from internal TMS, and ^{19}F spectra in p.p.m. upfield from internal $CFCl_3$. All signals are multiplets apart from the ^1H resonance at 1.58 which is a singlet. The ^{19}F signals are of equal area within a given spectrum.

identified as 5,10-dihydro-5,10-dimethyloctafluoroarsanthrene (1.5 g, 65%), m.p. 165°.

When $AsCl_3$, $SbCl_3$, $BiCl_3$, $C_6H_5PCl_2$, or $C_6H_5AsI_2$ were used as reactants, suspensions or solutions in THF were employed.

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1 F.G. Mann, The heterocyclic derivatives of phosphorus, arsenic and bismuth, Wiley-Interscience, New York, N.Y. 1970.

2 C. Tamborski and E.J. Soloski, J. Organometal. Chem., 20 (1969) 245.

3 J. Chatt and F.G. Mann, J. Chem. Soc., (1940) 1184.

4 F.G. Mann, J. Chem. Soc., (1963) 4266.

5 O. Kennard, F.G. Mann, D.G. Watson, J.K. Fawcett, and K.A. Kerr, Chem. Commun. (1968) 269.

6 F.W.B. Einstein, personal communication.

7 K. Mislow, A. Zimmerman, and J.T. Mellilo, J. Am. Chem. Soc., 85 (1963) 594.

8 J.E. Stuckey, A.W. Cordes, L.B. Handy, R.W. Perry, and C.K. Fair, Inorg. Chem., 11 (1972) 1846.

9 R.J. Holliday, R.W. Broach, L.B. Handy, A.W. Cordes, and L. Thomas, Inorg. Chem., 11 (1972) 1849.

10 W.K. Grindstaff, A.W. Cordes, C.K. Fair, R.W. Perry, and L.B. Handy, Inorg. Chem., 11 (1972) 1852.

11 A. Camerman and J. Trotter, J. Chem. Soc., (1965) 730.