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Pentafluorophenylarsenic Derivatives

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THERE has recently been considerable interest in pentafluorophenylphosphorus compounds, but little has been reported on the chemistry of the corresponding arsenic derivatives. We report some of our results concerning $(C_6F_5)_2As$ and C_6F_5As derivatives, which show interesting differences on comparison with the corresponding phosphorus derivatives.

The arsenic chlorides, $C_6F_5AsCl_2$ (b.p. 52°/0·1 mm.) and $(C_6F_5)_2AsCl$ (b.p. 82°/0·1 mm.), were made by reaction of C_6F_5MgBr with $AsCl_3$ or $Me_2N,AsCl_2$, respectively. Treatment of pentafluorophenylarsonous dichloride with mercury gave a benzene-soluble compound, which after recrystallisation from benzene–petroleum ether was characterised by elemental analyses and molecular weight measurements [Found: 952 ($CHCl_3$), 968 (mass-spectroscopy); Calc. for $(C_6F_5As)_4$: 968] as the tetramer $(C_6F_5As)_4$, m.p. 141°. The molecular formula agrees with the ^{19}F n.m.r. spectrum, which showed the expected pattern for a C_6F_5X derivative with peaks centred at 125·9, 152·1, and 161·8 p.p.m. of intensities 2 : 1 : 2. The *ortho*-fluorines at low field showed evidence of ^{75}As quadrupolar broadening.

The phosphorus compounds, $C_6F_5PCl_2$ and $C_6F_5PBr_2$, form the pentamer $(C_6F_5P)_5$[1] on reaction with mercury and it is interesting that the only previously reported[2] As_4 ring compound is $(CF_3As)_4$. The corresponding methylarsenic and phenylarsenic homocyclic compounds have been shown by *X*-ray crystallography to be $(MeAs_5)$ and $(PhAs_6)$, respectively.[3]

Bis(pentafluorophenyl)arsinous chloride reacts with mercury to afford tetrakis(pentafluorophenyl)diarsine, $(C_6F_5)_2AsAs(C_6F_5)_2$, which after recrystallisation from benzene 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 at 133·5, 146·6, 152·0, 160·0, and 162·8 p.p.m., which is clearly inconsistent with the molecular formula $(C_6F_5)_2AsAs(C_6F_5)_2$. Sublimation of the diarsine *in vacuo* resulted in the separation of two isomers of tetrakis(pentaphenyl)diarsine. The ^{19}F n.m.r. spectrum of each isomer showed three peaks of relative intensity 2 : 1 : 2, which occurred at133·5, 152·0, and 162·8 p.p.m. for the isomer subliming at 140°, and at 133·5, 146·6, and 160·0 p.p.m. for the isomer subliming at 230°. Examination of models suggests that the two isomers are rotamers, possibly *trans*- and *gauche*-forms of $(C_6F_6)_2As$-$As(C_6F_5)_2$. The implied high energy barrier for the interconversion of the two isomers probably arises because of a balance of two factors. (i) Steric hindrance due to the *ortho*-fluorines, and (ii) the As–As bond distance, which is of the correct length to allow the formation of a *gauche*-form, but not of great enough length to allow free rotation. Alternative routes to the diarsine, *e.g.*, the reaction of $(C_6F_5)_2AsCl$ with $(CH_3)_3SiH$ or the reaction of

$(C_6F_5)_2As{\cdot}S{\cdot}As(C_6F_5)_2$ with mercury gave similar mixtures of the two isomers.

Reaction of the As—As compounds with aqueous alkali gave a quantitative yield of pentafluorobenzene, and reaction with an excess of chlorine proceeded slowly to give C_6F_5Cl.

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