Studies on the Symmetrical Diphosphines and Diarsines, $(F_3C)(R)E{\cdot}E(R)(CF_3)$, where E = P or As, R = H or Me

By ROBERT C. DOBBIE* and PETER D. GOSLING

(*Department of Inorganic Chemistry, The University of Newcastle upon Tyne, Newcastle upon Tyne* NE1 7RU)

Summary The novel compound 1,2-bis(trifluoromethyl)-diarsine, $(F_3C)(H)As{\cdot}As(H)(CF_3)$, and the corresponding diphosphine can be prepared by reduction of F_3CEI_2 (E = As or P) by mercury and a deficiency of HI; the methyl derivatives, $(F_3C)(Me)E{\cdot}E(Me)(CF_3)$ have also been prepared.

FEW 1,2-disubstituted diphosphines have been characterised.[1] Of particular interest in view of its thermal stability is 1,2-bis(trifluoromethyl)diphosphine, $(F_3C)(H)$-$P{\cdot}P(H)(CF_3)$, (I), originally prepared[2] by controlled hydrolysis of $(F_3CP)_4$. We now report a simpler preparation of (I), the preparation of the novel 1,2-disubstituted diarsine, $(F_3C)(H)As{\cdot}As(H)(CF_3)$ (II), and studies on their 1,2-substituted methyl derivatives.

Reaction of F_3CEI_2 (E = P or As) with an excess (> 2 mol) of anhydrous HI and mercury gives F_3CEH_2 in almost quantitative yield.[3] However, when the reduction is attempted with a deficiency of HI (*ca.* 1 mol), F_3CEH_2 is formed along with the cyclic compounds $(F_3CE)_n$ (n = 4 and 5) and the compounds $(F_3C)(H)E{\cdot}E(H)(CF_3)$ [(I), E = P; (II), E = As] (20—40%). The diphosphine and diarsine are readily separated from the other products by fractionation under reduced pressure and may be identified by their chemical and spectroscopic properties. Compounds (I) and (II) react with HI according to the equations (1) and (2).

$$(F_3C)(H)E{\cdot}E(H)(CF_3) + HI \rightarrow F_3CEH_2 + F_3CEHI \tag{1}$$

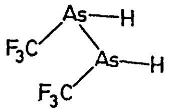
$$2F_3CEHI \rightleftharpoons F_3CEH_2 + F_3CEI_2 \tag{2}$$

Both F_3CPHI[4] and F_3CAsHI disproportionate so that the products isolated from (II) (1 mol) are F_3CAsH_2 (1·31 mol), F_3CAsHI (0·40 mol), and F_3CAsI_2 (0·31 mol), establishing the empirical formula of the diarsine. Compound (II) decomposes in the liquid phase below room temperature to give F_3CAsH_2 and $(F_3CAs)_n$ ($n = 4$ or 5) although an equilibrium concentration of the diarsine remains, as has been established by mixing F_3CAsH_2 with $(F_3CAs)_n$ at room temperature, equation (3). By contrast, the diphosphine (I) is stable at room temperature although prolonged

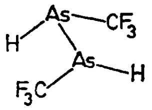
$$nF_3CAsH_2 + (F_3CAs)_n \rightleftharpoons n[(F_3C)(H)As]_2 \tag{3}$$

heating at 225 °C led the original workers to recognise two decomposition routes, giving some $(F_3C)_2PH$ and PH polymer as well as F_3CPH_2 and $(F_3CP)_4$.[2] An equilibrium analogous to that of equation (3) could not be established by heating F_3CPH_2 with $(F_3CP)_n$ at up to 180 °C.[5] This finding is in keeping with the expected much reduced basicity of F_3CPH_2 compared with F_3CAsH_2, or with $PhPH_2$, which equilibrates[1a] with $(PhP)_5$ in a manner similar to equation (3).

In an MeCN solution of (II), the absorptions in the ^{19}F n.m.r. spectrum due to the *meso*-(IIA) and (±)-(IIB) diastereoisomers (shown for clarity in eclipsed configuration) are resolved, giving two 'N doublets'[6] of unequal intensity at ϕ 39·26 p.p.m., *N* 11·6 Hz; and at ϕ 39·45, *N* 10·5, along with other symmetrically placed lines within each doublet, as expected if each isomer forms an $[AX_3]_2$ spin system ($A = {}^1H$; $X = {}^{19}F$).† In CCl_3F solution, the chemical shift of the isomers is within 0·02 p.p.m. The effect of MeCN on the ^{19}F n.m.r. spectra of fluorocarbon phosphines has been noted previously.[7] The ^{19}F resonances of the isomers of (I) are reported[1b] to be separated by 0·6 p.p.m.



(IIA)



(IIB)

A comparison of the ^{19}F n.m.r. spectra of (I) and (II) with the methyl substituted diphosphine and diarsine, $(F_3C)(Me)$-$E{\cdot}E(Me)(CF_3)$ [(III), E = P; (IV), E = As] is interesting. The diphosphine, originally reported by Burg *et al.*,[8] has now been more conveniently prepared by the action of dimethylmercury on F_3CPI_2. The ^{19}F n.m.r. spectrum of (III) in CCl_3F at 27 °C shows two well resolved $[AX_3]_2$ ($A = {}^{31}P$; $X = {}^{19}F$) patterns at ϕ 53·5 and 54·8 p.p.m., while the new diarsine (IV), prepared by reduction of F_3CAs-(Me)I with mercury, gives widely separated singlets at ϕ 47·3 and 48·8 p.p.m. No H–F coupling is detected for (III) or (IV). The much larger chemical shift difference for the diastereoisomers of the methyl compounds compared to the hydrogen compounds is noteworthy.

(*Received*, 15*th May* 1975; *Com.* 553.)

---

† ϕ = 0·0 p.p.m. for CCl_3F.

[1] (a) J. P. Albrand and D. Gagnaire, *J. Amer. Chem. Soc.*, 1972, **94**, 8630; (b) J. P. Albrand, S. P. Anderson, H. Goldwhite, and L. Huff, *Inorg. Chem.*, 1975, **14**, 570.

[2] W. Mahler and A. B. Burg, *J. Amer. Chem. Soc.*, 1958, **80**, 6161.

[3] R. G. Cavell and R. C. Dobbie, *J. Chem. Soc.* (*A*), 1967, 1308.

[4] R. C. Dobbie and P. D. Gosling, *J.C.S. Dalton*, in the press.

[5] J. P. Albrand, personal communication.

[6] R. K. Harris. *Canad. J. Chem.* 1964, **42**, 2275.

[7] P. R. Mason, Ph.D. Thesis, University of Newcastle upon Tyne, 1974.

[8] A. B. Burg, K. K. Joshi, and J. F. Nixon, *J. Amer. Chem. Soc.*, 1966, **88**, 31.