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## 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

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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.<sup>1</sup> 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<sup>2</sup> by controlled hydrolysis of  $(F_3CP)_4$ . We now report a simpler preparation of (I), the preparation of the novel 1,2-disubstituted diarsine,  $(F_aC)(H)As \cdot As(H)(CF_a)$  (II), and studies on their 1,2-substituted methyl derivatives.

Reaction of  $F_3CEI_3$  (E = P or As) with an excess (> 2 mol) of anhydrous HI and mercury gives  $F_3CEH_3$  in almost quantitative yield.<sup>3</sup> However, when the reduction is attempted with a deficiency of HI (*ca.* 1 mol),  $F_3CEH_3$  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).

$$(F_{3}C)(H)E \cdot E(H)(CF_{3}) + HI \rightarrow F_{3}CEH_{2} + F_{3}CEHI$$
(1)

 $2F_{3}CEHI \Rightarrow F_{3}CEH_{2} + F_{3}CEI_{2}$ (2)Both F<sub>3</sub>CPHI<sup>4</sup> and F<sub>3</sub>CAsHI disproportionate so that the products isolated from (II) (1 mol) are F<sub>3</sub>CAsH<sub>2</sub> (1·31 mol), F<sub>3</sub>CAsHI (0.40 mol), and F<sub>3</sub>CAsI<sub>2</sub> (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

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

heating at 225 °C led the original workers to recognise two decomposition routes, giving some  $(\mathrm{F_{3}C})_{2}\mathrm{PH}$  and  $\mathrm{PH}$ polymer as well as  $F_3CPH_2$  and  $(F_3CP)_4$ .<sup>2</sup> 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.<sup>5</sup> This finding is in keeping with the expected much reduced basicity of F<sub>3</sub>CPH<sub>2</sub> compared with F<sub>3</sub>CAsH<sub>2</sub>, or with PhPH<sub>2</sub>, which equilibrates  $^{18}$  with  $(\mathrm{PhP})_{5}$  in a manner similar to equation (3).

In an MeCN solution of (II), the absorptions in the <sup>19</sup>F n.m.r. spectrum due to the meso-(IIA) and  $(\pm)$ -(IIB) diastereoisomers (shown for clarity in eclipsed configuration) are resolved, giving two 'N doublets'6 of unequal intensity at  $\phi$  39.26 p.p.m., N 11.6 Hz; and at  $\phi$  39.45, N 10.5, along with other symmetrically placed lines within each doublet, as expected if each isomer forms an [AX<sub>3</sub>]<sub>2</sub> spin system  $(A = {}^{1}H; X = {}^{19}F)$ , In CCl<sub>3</sub>F solution, the chemical shift of the isomers is within 0.02 p.p.m. The effect of MeCN on the <sup>19</sup>F n.m.r. spectra of fluorocarbon phosphines has been noted previously.7 The 19F resonances of the isomers of (I) are reported<sup>1b</sup> to be separated by 0.6 p.p.m.



A comparison of the <sup>19</sup>F n.m.r. spectra of (I) and (II) with the methyl substituted diphosphine and diarsine, (F<sub>3</sub>C)(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<sub>3</sub>CPI<sub>2</sub>. The <sup>19</sup>F n.m.r. spectrum of (III) in CCl<sub>3</sub>F at 27 °C shows two well resolved [AX<sub>3</sub>]<sub>2</sub>  $(A = {}^{31}P; X = {}^{19}F)$  patterns at  $\phi$  53.5 and 54.8 p.p.m., while the new diarsine (IV), prepared by reduction of F<sub>3</sub>CAs-(Me)I with mercury, gives widely separated singlets at  $\phi$  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.

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 $\dagger \phi = 0.0$  p.p.m. for CCl<sub>s</sub>F.

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