# An Electron Spin Resonance Study of Fluoroalkoxy- and Fluoroalkylphosphoranyl Radicals

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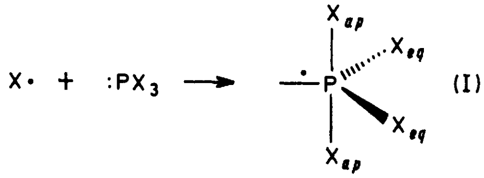
Two series of phosphoranyl radicals, containing fluoroalkoxy or trifluoromethyl ligands, respectively, have been generated in solution by radical addition to trivalent phosphorus compounds, and their e.s.r. spectra have been studied. The spectra of the radicals $R_FO\dot{P}(OR)_3$ and $R_FO\dot{P}Me(OR)_2$ exhibit large isotropic phosphorus hyperfine splittings and long-range fluorine coupling with (in many cases) fewer than the maximum number of chemically equivalent $^{19}F$ nuclei. Temperature-dependent line-shape changes were observed and interpreted in terms of the presence of rapid conformational equilibria. The e.s.r. spectra were consistent with trigonal bipyramidal structures for the phosphoranyl radicals, in which the $R_FO$ ligands are apical and the $CH_3$ groups equatorial.

The structures of the trifluoromethylphosphoranyl radicals, assigned on the basis of their e.s.r. spectra, show that the apicophilicity of the $CF_3$ group is less than that of Cl and usually greater than that of RO. Phosphoranyl radicals containing an apical $CF_3$ ligand exhibit lower values of *a*(P) than their methylphosphoranyl analogues, although the group electronegativity of $CF_3$ is much greater than that of $CH_3$. Temperature-dependent line-shape effects demonstrate that rotation about the P–$CF_3$ bond is restricted to a degree dependent upon the nature of the other substituents. Trifluoromethyl radicals add reversibly to trialkyl phosphites.

It is now well established that a variety of free radicals undergo rapid addition to trivalent phosphorus compounds to produce phosphoranyl radicals (I) [equation (i)], which generally adopt quasi-trigonal bipyramidal structures for which we may identify two types of ligand site, apical and equatorial.[1,2]

E.s.r. spectroscopy has proved an important technique for elucidating the structures and chemical transformations of phosphoranyl radicals, and such spectroscopic studies have identified many similarities between phosphoranyl radicals and the related diamagnetic phosphoranes, $PX_5$.



(I) (i)

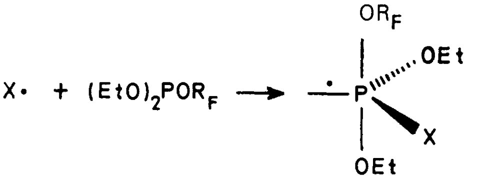
The e.s.r. spectra of a number of alkyl- and alkoxyphosphoranyl radicals in fluid solution have been described,[3-5] and it has been demonstrated that substituent electronegativity is a major factor in governing ligand apicophilicity (the preference of a ligand for an apical rather than an equatorial site). There is also evidence that the fragmentation of phosphoranyl radicals is configurationally selective, that is the rate of bond cleavage depends upon whether the substituent involved is at an apical or an equatorial site.[5]

Fluoroalkyl groups exhibit profoundly different electronic properties from their hydrocarbon analogues and we felt it would be of interest to examine by e.s.r. spectroscopy the formation and structures of a series of fluoroalkyl- and fluoroalkoxyphosphoranyl radicals.

## RESULTS AND DISCUSSION

(a) *Phosphoranyl Radical Generation.*—The radicals described below were produced directly in the cavity of the e.s.r. spectrometer by addition of photochemically generated methyl (from MeN:NMe), trifluoromethyl (from $CF_3I + Me_3Sn{\cdot}SnMe_3$), ethoxyl (from EtO·OEt), t-butoxyl (from $Bu^tO{\cdot}OBu^t$), perfluoro-t-butoxyl[6] (from t-$C_4F_9O{\cdot}OC_4F_9$-t) and trimethylsilyloxyl radicals[7] (from $Me_3SiO{\cdot}OSiMe_3$) to the appropriate trivalent phosphorus compound, usually in cyclopropane as solvent.

(b) *Fluoroalkoxyphosphoranyl Radicals.*—The fluoroalkoxyphosphoranyl radicals (1)—(4) (Table 1) were generated by addition of methyl radicals to the appropriate phosphite ester [equation (ii), X = Me]. These radicals exhibit phosphorus hyperfine coupling constants which are appreciably greater than that of the unfluorinated analogue[3] $Me\dot{P}(OEt)_3$ [*a*(P) 787 G at 203 K], and values of *a*(P) for (1)—(4) increase with the degree of fluorination of the ligand. These results agree with the trends established previously[1,3-5,8] which indicate that the isotropic phosphorus splitting for a phosphoranyl radical increases with ligand electronegativity, provided that the more electronegative ligands occupy apical



(II) (ii)

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[1] J. W. Cooper, M. J. Parrott, and B. P. Roberts, *J.C.S. Perkin II*, 1977, 730.

[2] W. G. Bentrude in ' Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, 1973, vol. 2, ch. 22.

[3] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 2224.

[4] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

[5] J. W. Cooper and B. P. Roberts, *J.C.S. Perkin II*, 1976, 808.

[6] A. G. Davies, R. W. Dennis, B. P. Roberts, and R. C. Dobbie, *J.C.S. Chem. Comm.*, 1974, 468.

[7] P. G. Cookson, A. G. Davies, N. A. Fazal, and B. P. Roberts, *J. Amer. Chem. Soc.*, 1976, **98**, 616.

[8] R. W. Dennis and B. P. Roberts, *J.C.S. Perkin II*, 1975, 140.

sites, and we assume that in (II; X = Me) the fluoroalkoxy-group is apical. The e.s.r. spectrum of the radical $(CF_3)_3CO\dot{P}F_3$ is also consistent with the presence of an apical $R_FO$ group.[9]

Only six of the nine fluorine nuclei in (1) give rise to resolvable coupling, even at the highest accessible temperature (200 K). A similar effect has been observed by Morton and his co-workers in the e.s.r. spectra of $(CF_3)_3CO\dot{P}F_3$ [9] [$a$(F) 9.1 G (6F)] and $(CF_3)_3CO\dot{S}F_4$ [10] [$a$(F) 6.6 G (6F)]. The e.s.r. spectrum of (2) exhibits coupling to only one spin-$\frac{1}{2}$ nucleus at low temperatures, and this splitting was shown to be due to fluorine rather than to a proton by generation of the deuteriated analogue (3). At higher temperatures splitting from two apparently equivalent fluorine nuclei was detected for (2) and (3), indicating that fluorine exchange occurs on the e.s.r. time-scale. At 243 K the radical (4) shows splitting from two apparently equivalent fluorine nuclei, although below 190 K the central line of the 1 : 2 : 1 triplet becomes broader than the wing lines, showing that these nuclei are in fact non-equivalent. For none of the radicals (1)—(4) could we resolve splitting from the equatorial methyl ligand,[3] and we conclude that the methyl group occupies an equatorial site.

TABLE 1

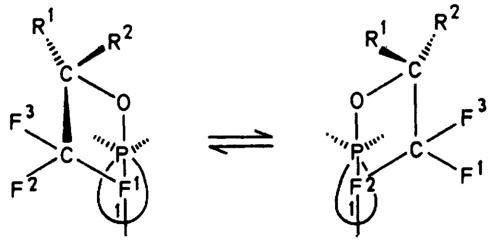
E.s.r. parameters for fluoroalkoxyphosphoranyl radicals $(EtO)_2\dot{P}(X)OR_F$ (II) in cyclopropane solution

| | | | | Hyperfine splittings (G) | |
|---|---|---|---|---|---|
| Radical | X | $R_FO$ | $T$/K | $a$(P) [a] | $a$(F) |
| (1) | Me | $(CF_3)_3CO$ | 153 | 878 | 10.0 (6F) |
| (2) | Me | $(CF_3)_2MeCO$ | 143 | | 9.5 (1F) |
| | | | 183 | 837 | 5.0 [b] (2F) |
| (3) | Me | $(CF_3)_2CD_3CO$ | 154 | | 9.5 (1F) |
| | | | 182 | 838 | 5.0 [b] (2F) |
| (4) | Me | $CF_3Me_2CO$ | 173 | 823 | 4.7 [b] (2F) |
| | | | 243 | | 5.5 (2F) |
| (5) [c] | EtO | $(CF_3)_3CO$ | 183 | 1 020 | 9.9 (6F) |
| (6) [d] | MeO | $(CF_3)_3CO$ | 183 | 1 021 | 10.5 (6F) |
| (7) | Bu$^t$O | $(CF_3)_3CO$ | 163 | 1 018 | 6.7 (6F) |
| (8) | Pe$^t$O | $(CF_3)_3CO$ | 163 | 1 018 | 6.5 (6F) |
| (9) [e] | EtO | $(CF_3)_2MeCO$ | 188 | 974 | 6.8 (2F) |
| (10) [e] | EtO | $(CF_3)_2CD_3CO$ | 152 | 969 | 11.3 (1F) |
| | | | 200 | 973 | 6.5 (2F) |
| (11) [e] | EtO | $CF_3Me_2CO$ | 152 | 926 | 4.2 [b] (2F) |
| | | | 178 | 929 | 4.4 (2F) |
| (12) | EtO | $CF_3CH_2O$ | 142 | 909 | 3.8 (2F) |
| | | | 246 | 909 | 2.5 (3F) |
| (13) | EtO | $CH_2FCH_2O$ | 163 | 887 | Not resolved [f] |
| | | | 228 | 888 | 2.3 (1F) |

[a] Obtained by using the Breit–Rabi equation: all $g$ factors were 2.003 ± 0.001. [b] Central component of the 1 : 2 : 1 triplet was broader than the wing lines. [c] The same spectrum was obtained either by photolysis of diethyl peroxide in the presence of $(CF_3)_3COP(OEt)_2$ or by photolysis of $(CF_3)_3CO{\cdot}OC(CF_3)_3$ in the presence of $(EtO)_3P$ in 1 : 1 cyclopropane–$CF_2ClCCl_2F$. The radical $CH_3\dot{C}HOP(OEt)_2$ was also detected in the latter system (see ref. 6). [d] Radical (6) is $(MeO)_3\dot{P}OC(CF_3)_3$, generated by photolysis of $(CF_3)_3CO{\cdot}OC(CF_3)_3$, in the presence of $(MeO)_3P$ in 1 : 1 cyclopropane–$CF_2ClCCl_2F$. The radical $\dot{C}H_2OP(OMe)_2$ was also detected (see ref. 6). [e] Minor concentrations of two other phosphoranyl radicals were also detected. These were identified as $(R_FO)_2\dot{P}(OEt)_2$ and $(EtO)_4P\cdot$ on the basis of their $^{31}P$ hyperfine splittings. Their origin is not clear, although a small amount of disproportionation of $R_FOP(OEt)_2$ is a possibility. [f] Peak–peak line-width was 8 G.

The spectra of the phosphoranyl radicals (II; X = RO) exhibit the same general features as those of the methyl radical adducts. The phosphorus splitting constants are all greater than that for $(EtO)_4P\cdot$ [$a$(P) 885 G at 203 K],[3] and the magnitudes increase with the number of fluorine atoms in, and thus the electronegativity of, the fluoroalkoxy-group. The value of $a$(P) for the $(EtO)_3\dot{P}OC(CF_3)_3$ radical (5) is similar to those for $Bu^tO(EtO)_2\dot{P}Cl$ (1037 G) [11] and $(EtO)_3\dot{P}OP(O)(OEt)_2$ (1039 G).[12] Coupling with fewer than the maximum number of fluorine nuclei was often observed, and for (9)—(11) line-shape changes were detected which indicate that exchange of two non-equivalent fluorine atoms is taking place on the e.s.r. time-scale. At high temperature the spectrum of (12) shows coupling to all three fluorine nuclei, but as the temperature was lowered the more intense components of the 1 : 3 : 3 : 1 quartets broadened, and at 142 K the spectrum appeared as a doublet ($^{31}P$ splitting) of triplets resulting from coupling with two apparently equivalent fluorine nuclei.

We suggest the following general explanation of the above phenomena. Possibly for electronic rather than steric reasons, one fluorine atom of the apical fluoroalkoxy-group is held in a position which results in a relatively large long-range hyperfine interaction with this nucleus [see equation (iii)]. Intramolecular exchange of this unique fluorine nucleus with another in the same trifluoromethyl group can occur without free rotation about the C–C bond of the $R_FO$ group [equation (iii)]. This exchange may result from a torsional motion about the $R_FO$–P bond.



(iii)

$R^1 = R^2 = CF_3$ } exchange (iii) is fast on the e.s.r. time-scale
$R^1 = R^2 = H$ } at all accessible temperatures

$R^1 = CF_3$, $R^2 = CH_3$ } exchange (iii) becomes slow on the e.s.r.
$R^1 = R^2 = CH_3$ } time-scale at low temperature

For the perfluoro-t-butoxyphosphoranyl radicals, both this type of exchange and rotation about the C–O bond (but not about the C–C bond) of the $R_FO$ group are rapid on the e.s.r. time-scale at all temperatures examined, resulting in resolvable splittings from six apparently equivalent fluorine nuclei. For the less symmetrical fluoroalkoxy-groups $(CF_3)_2MeCO$ and $(CF_3)Me_2CO$, rotation about the C–O bond can reasonably be expected to

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[9] A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Phys. Chem.*, 1975, **79**, 651.

[10] A. R. Gregory, S. E. Karavelas, J. R. Morton, and K. F. Preston, *J. Amer. Chem. Soc.*, 1975, **97**, 2206.

[11] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1339.

[12] A. G. Davies, M. J. Parrott, B. P. Roberts, and A. Skworonska, *J.C.S. Perkin II*, 1976, 1154.

involve a higher barrier, and thus for both classes of phosphoranyl radical either one or two fluorine nuclei give rise to resolvable splitting, depending upon whether the exchange shown in equation (iii) is slow or fast on the e.s.r. time-scale.

For the radical (12) the exchange shown in equation (iii) is rapid at all temperatures examined, but rotation about the $F_3C-C$ bond is now also sufficiently free that $F^1$, $F^2$, and $F^3$ are rendered equivalent on the e.s.r. time-scale at high temperatures.

Detailed molecular orbital calculations would be needed to substantiate these internally consistent proposals, but it is worth noting that the shortest P–F distance for the conformation shown in equation (iii) is favourable for interaction, and the relatively high stability of phosphoranes containing a five-membered ring system is well known.[13]

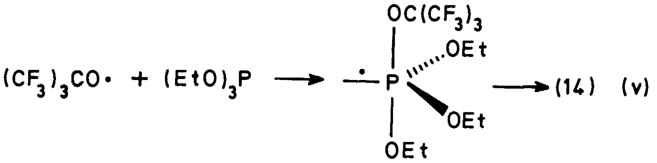
Computer simulation of the line-shape effects exhibited by (3), assuming exchange between two fluorine nuclei giving rise to splittings of 9.5 and 0.5 G, respectively, gave values of $k_{iii}$ between 160 and 188 K which are summarised in equation (iv) (where $\theta = 2.303RT$ kJ mol$^{-1}$).

For (3) at 173 K, $k_{iii} = 5.5 \times 10^7$ s$^{-1}$, whereas for

$$\log_{10} (k_{iii}/s^{-1}) = 10.7 - 9.8/\theta \qquad (iv)$$

(10) the value of $k_{iii}$ obtained by computer simulation was *ca.* $4 \times 10^8$ s$^{-1}$ (taking the fluorine splittings to be 11.3 and 1.7 G).

The phosphoranyl radical (5) was the only species detected initially when diethyl peroxide was photolysed in the presence of $(CF_3)_3COP(OEt)_2$; however after a short period of irradiation the spectrum of a second phosphoranyl radical (14) (Table 2) was observed [$a$(P) 825, $a$(F) 27.4 G (3F) at 173 K]. Identical primary (5) and secondary (14) phosphoranyl radicals were detected when perfluorodi-t-butyl peroxide was photolysed in the presence of triethyl phosphite [equation (v)].



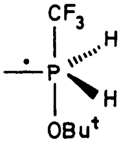
(v)

(5)

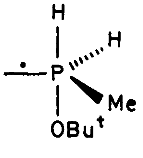
In a preliminary communication concerned mainly with the reactions of the perfluoro-t-butoxyl radical,[6] we tentatively assigned to (14) the structure $CF_3\dot{P}(OEt)_3$, but we now believe this assignment to be incorrect (see below). The radical (6) $[(MeO)_3\dot{P}OC(CF_3)_3]$ was the primary product of the reaction of perfluoro-t-butoxyl radicals with trimethyl phosphite, but a secondary radical (15), which exhibited spectroscopic parameters similar to those of (14) [$a$(P) 820, $a$(F) 26.0 G (3F) at 183 K], was also detected. The reaction of t-butoxyl or t-pentoxyl radicals with $(CF_3)_3COP(OEt)_2$ yielded, apart from the primary fluoroalkoxyphosphoranyl radicals, secondary species with phosphorus splittings similar to those of (14) and (15), and further fine structure which was interpreted in terms of a larger coupling to one fluorine and a smaller coupling to two equivalent fluorine nuclei. The secondary product (16), from the interaction of t-butoxy radicals with $(CF_3)_3COP(OEt)_2$, showed $a$(P) 807, $a$($F^1$) 38.0, $a$($F^2$) 23.8 G at 150 K. Since it appeared likely [6] to us that these secondary species were phosphoranyl radicals containing a trifluoromethyl ligand, we extended our study to include fluoroalkylphosphoranyl radicals.

(c) *Fluoroalkylphosphoranyl Radicals.*—Krusic, Mahler, and Kochi [4] did not detect any phosphoranyl radicals during the photolysis of di-t-butyl peroxide in the presence of tris(trifluoromethyl)phosphine: a strong spectrum of the trifluoromethyl radical, resulting from α-scission of the presumed phosphoranyl intermediate, was observed at all temperatures. We have confirmed that, even at 133 K in propane as solvent, the only spectrum detectable is that of $CF_3\cdot$, and clearly the phosphoranyl radical $(CF_3)_3\dot{P}OBu^t$ undergoes α-scission extremely rapidly.

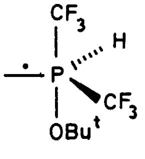
However, other phosphoranyl radicals proved more stable with respect to fragmentation and the spectroscopic parameters of a series of trifluoromethylphosphoranyl radicals are gathered in Table 2.



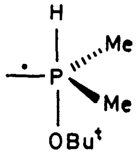
(18)



(19)



(20)



(21)

Photolysis of di-t-butyl peroxide in the presence of $CF_3PH_2$ gave rise to an intense e.s.r. spectrum assigned to the phosphoranyl radical (18) (see Figure). The proton splittings of 10.5 G indicate that the hydrogen ligands occupy equatorial sites,[4,14,15] and the $CF_3$ group must therefore be apical. Even at 173 K (see Figure) there is some selective broadening of the more intense components of the 1 : 3 : 3 : 1 quartets, resulting from coupling with the three fluorine nuclei, which we attribute to restriction of rotation about the apical P–C bond, and at lower temperatures this selective broadening becomes more marked.

The radical (18) exhibits much greater stability

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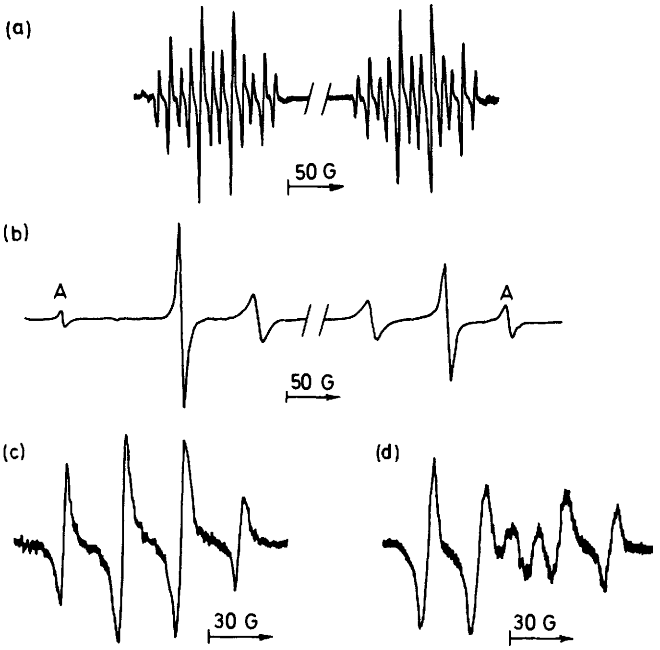
[13] B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, *J. Amer. Chem. Soc.*, 1971, **93**, 4004.

[14] M. C. R. Symons, *Mol. Phys.*, 1974, **27**, 785.

[15] A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Chem. Phys.*, 1975, **62**, 2004; K. Nishikida and F. Williams, *J. Amer. Chem. Soc.*, 1975, **97**, 5462.

towards loss of a trifluoromethyl radical than does $(CF_3)_3\dot{P}OBu^t$, and this seems likely to be in part a result of steric compression [absent in (18)] between the apical and equatorial $CF_3$ groups in the latter species.[5]



E.s.r. spectra of (a) the radical $CF_3\dot{P}(H_2)OBu^t$ (18) in propane at 173 K; (b) the radical $CF_3\dot{P}(OEt)_2OBu^t$ (26) in cyclopropane at 153 K [lines marked A are due to $Bu^tO\dot{P}(OEt)_3$ (see text)]; (c) the radical (14) [$CF_3\dot{P}(OEt)(X)(Y)$] in cyclopropane–$CCl_2FCF_2Cl$ (2 : 1 v/v) at 180 K {only the low-field [$M_I(^{31}P) = +\frac{1}{2}$] lines are shown}; and (d) the radical (16) [$CF_3\dot{P}(OBu^t)(X)(Y)$] in cyclopropane at 150 K {only the low-field [$M_I(^{31}P) = +\frac{1}{2}$] lines are shown}

The apicophilicity of the $CF_3$ group is apparently greater than that of a hydrogen atom, which is expected in view of the much higher electronegativity of the former ligand, but the phosphorus splitting in (18) is surprisingly small, being comparable with that for (19)[1,4] [$a$(P) 627, $a(H_{ap})$ + 139, $a(H_{eq})$ − 9.6, $a(CH_3)$ 3.9 G (3 H) at 183 K], in which the methyl group has a lower apicophilicity than hydrogen.

An additional line-width effect is apparent in the spectrum of (18) (see Figure). The inner lines of both the low-($\tilde{M}_{CF_3} + \frac{1}{2}, + \frac{3}{2}$) and high-($\tilde{M}_{CF_3} - \frac{1}{2}, - \frac{3}{2}$) field quartets are broadened relative to the outer lines (corresponding to $\tilde{M}_{CF_3} - \frac{1}{2}, - \frac{3}{2}$ and $+ \frac{1}{2}, + \frac{3}{2}$, respectively), and this differential line-broadening becomes more pronounced at lower temperatures. A similar line-width effect was observed in the spectra of all other trifluoromethylphosphoranyl radicals containing an apical $CF_3$ group, and we attribute this broadening to modulation of the anisotropic Zeeman interaction and fluorine and phosphorus hyperfine splittings by tumbling of the radical in solution.

The e.s.r. spectrum of the phosphoranyl adduct from t-butoxyl radicals and $(CF_3)_2PH$ was analysed in terms of structure (20). The central components of the quartets due to coupling with the apical $CF_3$ group are severely broadened at 143 K and are difficult to detect. At higher temperatures (20) undergoes rapid α-scission with loss of trifluoromethyl radicals. The spectrum of (20) also exhibits the line-shape effects described above for (18) and attributed to anisotropy of the Zeeman and hyperfine interactions. The phosphorus splitting in (20) is again surprisingly small when we consider the high electronegativity[16] of the $CF_3$ group (3.46) as compared with that of $CH_3$ (2.27). For comparison, the radical

TABLE 2

E.s.r. parameters for the trifluoromethylphosphoranyl radicals $CF_3\dot{P}ABC$ in cyclopropane solution

| | Substituents | | | | Hyperfine splittings (G) | | |
|---|---|---|---|---|---|---|---|
| Radical | A | B | C | $T$/K | $a$(P) [a] | $a(CF_3)$ [b] | Others |
| (18)[c] | H | H | $Bu^tO$ | 173 | 618 | 29.4 (3F) | 10.5 (2H) |
| (20)[c] | $CF_3$ | H | $Bu^tO$ | 143 | 627 | 28.2 (3F) | 10.7 (1H); 4.8 (3F) |
| (22) | $CF_3$ | Cl | $Bu^tO$ | 163 | 861 [d] | | 36.0 (1 $^{35}$Cl); 2.7 (6F) |
| (23) | Cl | Cl | $Bu^tO$ | 203 | 1 068 [e] | | 31.8 (2 $^{35}$Cl); *ca.* 2.6 (3F) |
| (24) | EtO | EtO | EtO | 173 | 658 | 66.3 (d) | |
| (25) | MeO | MeO | MeO | 190 | 663 | 64.5 (d) | |
| (26) | EtO | EtO | $Bu^tO$ | 173 | 650 | 68.3 (d) | |
| (27) | EtO | EtO | $(CF_3)_3CO$ | 182 | 742 | 60.3 (d) | 9.3 (6F) |
| (28)[f] | EtO | EtO | EtO | 152 | 662 | 28.0 (d) [f,g] | |
| (29) | $OCH_2{\cdot}CH_2O$ | | EtO | 179 | 688 | 59.4 (d) | 5.2 (1H) |
| (30) | $OCH_2{\cdot}CH_2O$ | | $Bu^tO$ | 188 | 673 | 58.3 (d) | 5.4 (1H) |
| (31) | $OCH_2{\cdot}CH_2O$ | | $Me_3SiO$ | 202 | 687 | 61.5 (d) | 5.7 (1H) |
| (14)[h] | ? | ? | EtO | 173 | 825 | 27.4 (3F) [i] | |
| (15) | ? | ? | MeO | 183 | 820 | 26.0 (3F) | |
| (16) | ? | ? | $Bu^tO$ | 150 | 807 | 38.0 (1F)<br>23.8 (2F) | |
| (17) | ? | ? | $Pe^t$ | 173 | 808 | 38.0 (1F)<br>24.0 (2F) | |

[a] Obtained by using the Breit–Rabi equation: all $g$ factors were 2.003 ± 0.001, unless otherwise stated. [b] Hyperfine splitting assigned to the apical trifluoromethyl group; '(d)' indicates a doublet splitting (see text). [c] In propane solvent. [d] $g$ 2.007. [e] $g$ 2.010. [f] Phosphoranyl radical $CF_3CF_2\dot{P}(OEt)_3$, generated by photolysis of $CF_3CF_2I + Me_3SnSnMe_3 + P(OEt)_3$ in cyclopropane. This radical exhibited a doublet splitting from fluorine. [g] $a$(F) = 25.3 G (d) (173 K), 24.2 G (d) (197 K). [h] The same species was obtained from photolysis of EtO·OEt in the presence of $(EtO)_2POC(CF_3)_3$ or photolysis of $(CF_3)_3CO{\cdot}OC(CF_3)_3$ in the presence of $(EtO)_3P$. [i] The central lines of the 1 : 3 : 3 : 1 quartet were broadened relative to the outer lines, as a result of restriction of rotation about the $F_3C–P$ bond.

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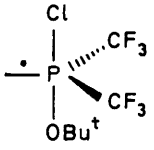
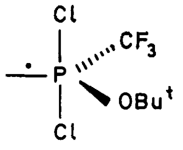
[16] J. E. Huheey, *J. Phys. Chem.*, 1965, **69**, 3284.

(21) exhibits[4] a phosphorus splitting of 632 G,* although the hydrogen ligand now occupies an apical site, as opposed to an equatorial site in (20). If we assume[1] that the detected isomer (20) is the most stable structure of the species $Bu^tO(CF_3)_2\dot{P}H$, the apicophilicity of $CF_3$ is apparently *less* than that of the t-butoxy-group in this radical.

Photolysis of di-t-butyl peroxide in the presence of $(CF_3)_2PH$ between 173 and 203 K yielded the spectrum of a second phosphorus-containing radical [$a$(P) 75.3, $a$(F) 14.0 G (3F) at 173 K] which we tentatively attribute to the phosphinyl radical $CF_3\text{–}\dot{P}\text{–}OBu^t$. This same spectrum, along with another [$a$(P) 93.5, $a$(F) 12.5 G (6F) at 173 K] assigned to $(CF_3)_2P\cdot$, was detected during photolysis of di-t-butyl peroxide in the presence of $(CF_3)_2P\text{–}P(CF_3)_2$ in propane as solvent.

The structures of the chlorophosphoranyl radicals (22) and (23), generated by addition of t-butoxy radicals to the appropriate chlorophosphines could be inferred from the magnitudes of the chlorine[11] and fluorine hyperfine splittings. In (22) the relative apicophilicities of $CF_3$ and $Bu^tO$ are again reversed as compared with the order in (18), and this is perhaps an indication of the similarities in the preferences of these two ligands for apical sites. However, monochlorophosphoranyl radicals may comprise a rather special class for which the structures deviate strongly from trigonal bipyrimidal and for which the unpaired electron is largely located in a P–Cl $\sigma^*$-orbital.[17] The phosphorus splittings for (22) and (23) are substantially *larger* than those for the unfluorinated analogues[11] [for $Et_2Cl\dot{P}OBu^t$, $a$(P) 794 G; for $MeCl_2\dot{P}OBu^t$, $a$(P) 1020 G]; however neither (22) nor (23) contains an apical $CF_3$ group (see below).


(22)

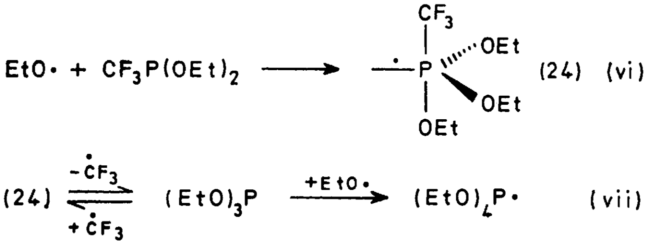

(23)

Freely rotating apical $CF_3$ groups appear to give rise to fluorine splittings of *ca.* 28 G (3F), whereas a splitting of 2.8—4.6 G (3F) is characteristic of an equatorial $CF_3$ ligand. For $Me_3\dot{P}OBu^t$ the apical and equatorial methyl proton coupling constants are 4.6 and 2.8 G, respectively.[4,5]

Photolysis of diethyl peroxide in the presence of $CF_3P(OEt)_2$ gave rise initially to one phosphoranyl radical (24), although the spectrum[3] of $(EtO)_4P\cdot$ [$a$(P) 884 G] as a secondary product [equations (vi) and (vii)] rapidly became apparent.

Since at all accessible temperatures (143—228 K) only two lines resulting from fluorine hyperfine interaction could be detected, we sought further evidence for the structure (24). The identical spectrum to that assigned to (24) was detected during photolysis of the mixtures (A)—(D) (in cyclopropane as solvent): all these experiments involve the generation of $CF_3\cdot$ in the presence of triethyl phosphite.

The e.s.r. spectrum of the trifluoromethyl radical, which was apparent in each of the above systems without $(EtO)_3P$, was partially or completely (at low temperatures and high phosphite concentrations) quenched in the presence of the phosphite, and replaced by the spectrum assigned to (24). We conclude that the addition of trifluoromethyl radicals to triethyl phosphite is readily reversible, as is the addition of methyl radicals.[5]



$$(24) \underset{+\dot{C}F_3}{\overset{-\dot{C}F_3}{\rightleftharpoons}} (EtO)_3P \xrightarrow{+EtO\cdot} (EtO)_4P\cdot \quad \text{(vii)}$$

(A) $CF_3I + Me_3SnSnMe_3 + (EtO)_3P$
(B) $CF_3I + (EtO)_3P$
(C) $(CF_3)_3P + Bu^tO\cdot OBu^t + (EtO)_3P$
(D)† $(CF_3)_3As + Bu^tO\cdot OBu^t + (EtO)_3P$

Similar species were obtained by addition of trifluoromethyl radicals to $(MeO)_3P$ [radical (25)] and of t-butoxyl radicals to $CF_3P(OEt)_2$ [radical (26)] (see Figure). The inner lines of the four-line spectra attributed to (24)—(26) were broader than the outer lines (see Figure), and for (24) at 167 K this differential line broadening increased with solvent viscosity, being much more pronounced in iso-octane than in cyclopropane. This is expected if broadening is the result of modulation of anisotropic Zeeman and hyperfine interactions by the tumbling of the radical in solution (see above). The radicals (24)—(26) all have phosphorus splitting constants which are much smaller than that for $Me\dot{P}(OEt)_3$ [$a$(P) 787 G at 203 K].[3] The magnitudes of the fluorine couplings are most consistent with apical placement of the $CF_3$ groups, and the doublet splitting indicates that rotation about the P–C bond is restricted, even at 228 K for (24).

Addition of trifluoromethyl radicals (from $CF_3I$ and $Me_3Sn\cdot SnMe_3$) to $(CF_3)_3COP(OEt)_2$ at 182 K gave rise to the spectrum of (27), which showed a doublet splitting [with differential line broadening similar to that exhibited by (24)—(26)] from the apical $CF_3$ group, and coupling to six apparently equivalent fluorine nuclei of the $(CF_3)_3CO$ ligand. A weak signal from the trifluoromethyl radical was also detected. The phosphorus splitting for (27) (742 G) is appreciably less than that

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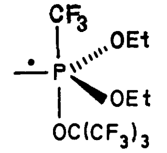
* This value is a line spacing and has not been corrected by using the Breit–Rabi equation; however the correction would be small.

† Only $CF_3\cdot$ radicals were detected during the photolysis of $Bu^tO\cdot OBu^t$ in the presence of $As(CF_3)_3$, at or above 143 K in propane, and no arsoranyl radicals were detected, even as secondary products[18] after prolonged irradiation.

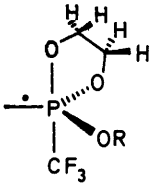
[17] M. C. R. Symons, *Chem. Phys. Letters*, 1976, **40**, 226; T. Berclaz, M. Geoffroy, and E. A. C. Lucken, *ibid.*, 1975, **36**, 677.

[18] A. G. Davies, D. Griller, and B. P. Roberts, *J. Organometallic Chem.*, 1972, **38**, C8.

for (1) (878 G). The relationship between group electronegativity [16] and the isotropic phosphorus hyperfine splitting, which appears to hold so well for other ligands,[1,4,8] breaks down when an apical CF$_3$ group is present. It seems reasonable that an electronic interaction should exist for trifluoromethylphosphoranyl radicals which contain an apical CF$_3$ group such that unpaired electron density is transferred from phosphorus into fluorine 2*p* orbitals. Recent results which indicate that the inductive effect of a CF$_3$ substituent in an organic molecule is a ' through-space ' rather than a ' through-bond ' interaction may also be important in this context. Although a CF$_3$ substituent polarises the electrons of a benzene ring such that the point of attachment bears a relatively high negative charge, the trifluoromethyl group in fact *donates* electron density to the ring.[19] How relevant these observations are to phosphoranyl radicals is uncertain, however, and detailed molecular orbital calculations would be helpful.



(27)



(29) R = Et
(30) R = Bu$^t$
(31) R = Me$_3$Si

Addition of perfluoroethyl radicals to triethyl phosphite yielded the radical (28), which appears, by analogy with the species containing CF$_3$ ligands, to possess an apical perfluoroethyl group giving rise to a doublet splitting because of restricted rotation, although the magnitude of this splitting is much smaller than that for (24).

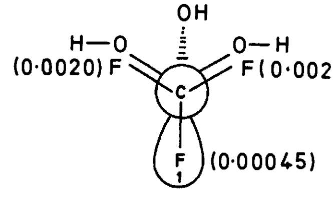
Incorporation of two ligands into a five-membered ring often appreciably modifies the properties of a phosphoranyl radical.[1,20] However, the spectra of the cyclic radicals (29) and (30) were very similar to those of their acyclic analogues (24) and (26), and may be interpreted in terms of the structures shown.

The spectrum of the trimethylsilyloxyl analogue (31) was similar. The radical (29) was much more stable towards loss of CF$_3$· than was (24), and the spectrum of the former could still be observed at 268 K, at which temperature still only a doublet splitting from the CF$_3$ group was detected. In addition, at 268 K coupling with only one ring proton was observed, indicating that exchange of apical with equatorial endocyclic ligands [M4 (ring) exchange [1]] was slow on the e.s.r. time-scale at this temperature.[1]

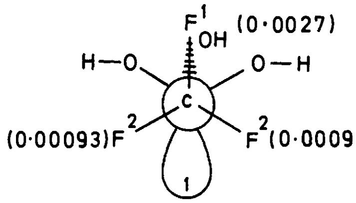
If the doublet fluorine splitting detected for (29) results from an intermediate rate of rotational modulation of the splittings from the CF$_3$ group, then we would expect to see some changes in the spectrum over the temperature range 178—268 K. In addition, it seems unlikely that for all the radicals CF$_3\dot{P}$(OEt)$_2$OR the spectra should appear in the intermediate exchange region, despite variations in the nature of R. Hence, we prefer to assign the doublet splitting in the spectra of (24)—(27) and (29)—(31) to a unique fluorine nucleus in a conformation held rigidly on the e.s.r. time-scale. The other two fluorine nuclei would give rise to splittings which are unresolved within the line-width (usually *ca.* 3—5 G). The barrier to rotation about the apical P–C bond increases on going from (18) (with two equatorial hydrogen ligands) to (24) (with two equatorial ethoxy-groups), in line with a predominantly steric origin.

In order to investigate briefly the magnitude of the barrier to rotation about the P–C bond, INDO molecular orbital calculations were carried out for the ' eclipsed ' and ' staggered ' conformations, (a) and (b), of CF$_3$-$\dot{P}$(OH)$_3$ with an apical CF$_3$ group.*

The rotamer (b) is calculated to be more stable than (a) by 7.4 kJ mol$^{-1}$ and probably represents the most stable conformation about the P–C bond. The figures in parentheses are $^{19}$F 2*s* orbital spin densities (after spin-annihilation—those before were very similar). Taking the coupling for unit electron population of the $^{19}$F 2*s* orbital to be 17 200 G, the unpaired electron density on the unique fluorine nucleus in (b) corresponds to a hyperfine splitting of 46 G.



(a)



(b)

We are now in a position to discuss the nature of the secondary phosphoranyl radicals (14)—(17), which are formed in systems where (CF$_3$)$_3$CO$\dot{P}$(OR)$_3$ is generated. The fluorine splitting for the radical (15), derived from the reaction of perfluoro-t-butoxyl radicals with trimethyl phosphite, clearly shows that this species has an apical CF$_3$ group, and rotation about the P–CF$_3$ bond is essentially free at 183 K. A similar species, (14), was detected in the reaction of perfluoro-t-butoxyl radicals with triethyl phosphite, and (14) was also detected as a secondary product when ethoxyl radicals reacted with (CF$_3$)$_3$COP(OEt)$_2$. At 180 K, the central components

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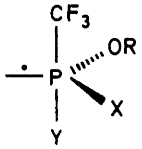
* We are grateful to Dr. A. Hudson for carrying out these calculations; bond lengths: P–C, 1.90; P–O, 1.65; C–F, 1.36; O–H, 0.96 Å; bond angles: CPO$_{ap}$ 180°; O$_{eq}$PO$_{eq}$ 100°; O$_{eq}$PC 90°; O$_{eq}$PO$_{ap}$ 90°; all other bond angles taken as 109.5°.

[19] S. A. Holmes and T. D. Thomas, *J. Amer. Chem. Soc.*, 1975, **97**, 2337.

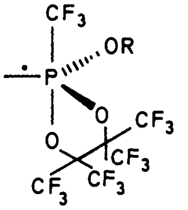
[20] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1416.

of the 1 : 3 : 3 : 1 quartet were broader than the wing lines (see Figure), indicating the onset of incomplete rotational averaging of the splittings from the three fluorine nuclei. The spectra of (16) and (17), derived indirectly from the interaction of t-butoxyl and t-pentoxyl radicals, respectively, with $(CF_3)_3COP(OEt)_2$, showed that the rate of rotation about the $F_3C$–P bond was such that the slow exchange limit was approached, and two different fluorine splittings were detected (Table 2). These results lead us to conclude that (14)—(17) have structures of the type (III; R = Me, Et, $Bu^t$, or t-pentyl).

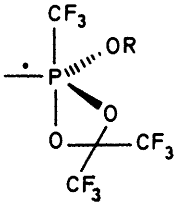
Comparison of the phosphorus splittings for (26) and (27) with those of (14)—(17) indicates that X and Y are



(III)



(IV)



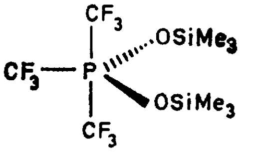
(V)

most probably fluoroalkoxy-ligands, and both the absence of long-range fluorine coupling [see section (b)] and the nature of the reagents which lead ultimately to (14)—(17), suggest structures of the types (IV) and (V).

The radicals (IV) and (V) might possibly be produced from $(CF_3)_3CO\dot{P}(OR)_3$ by a series of reactions involving initial intramolecular transfer of a $CF_3$ group from carbon to phosphorus, but so far our attempts to generate species such as (IV) and (V) by independent routes have not been successful.

Using the fluorine splittings obtained for (16) and (17), computer simulation of the spectrum of (14) indicates that the rate constant for rotation about the $F_3C$–P bond is *ca.* $2 \times 10^8$ $s^{-1}$ at 180 K. It might appear surprising that the fluorine splittings for (16) and (17) should be similar in magnitude, whereas for (24)—(27) and (29)—(31) we have suggested that they are very different [58—68 (1F) and $\leqslant 5$ G (2F)]. However, the electronic structures and the most stable conformations of the radicals (IV) and (V) could be rather different from those of the species not containing a fluorinated ring system.

On the basis of n.m.r. studies of a series of phosphoranes containing trifluoromethyl ligands,[21] it has proved possible to establish the relative apicophilicity of the $CF_3$ group. It has been concluded that the trifluoromethyl group is intermediate in apicophilicity between chloro- and alkoxy-ligands, the order of decreasing apicophilicity being F,Cl > $CF_3$ > MeO,$Me_3SiO$,MeS > H,$CH_3$,$Me_2N$. Below 133 K, the $^{19}F$ n.m.r. spectrum of the phosphorane (32) exhibits changes



(32)

ascribed to freezing of rotation about the apical P–C bond, such that there are two equivalent fluorine nuclei and one unique.[21a] Rotation about the equatorial C–P bond does not appear to be restricted on the n.m.r. time-scale at these temperatures.

The position of $CF_3$ in the apicophilicity series for phosphoranyl radicals is thus the same as for the related phosphoranes, that is between Cl and RO. However, for the phosphoranyl radicals the differences in apicophilicity appear to be less marked, and in radicals (20) and (22) the alkoxy-group occupies an apical site in preference to a $CF_3$ group. For both phosphoranes and phosphoranyl radicals the barrier to rotation about the apical P–$CF_3$ bond is probably essentially steric in origin.

## EXPERIMENTAL

*E.s.r. Studies.*—Spectra were recorded with a Varian E-4 X-band spectrometer equipped for high-intensity u.v. irradiation of samples in the cavity.[1,3,8] Unfiltered light, from a Philips SP 500 0.5 kW A.C. high-pressure mercury discharge lamp, was focused onto the sample, contained in the standard variable-temperature Dewar insert, through two fused silica lenses and a water-filled cell with silica end plates. The incident intensity could be varied by means of a series of wire gauze screens. The temperature (±2 °C) of the sample was measured by means of a thermocouple placed alongside the sample tube, and frequently calibrated against a second thermocouple contained in a sample tube in the sensitive region of the cavity. The heating effect of the u.v. irradiation was estimated by measuring the β-proton coupling constant of the isobutyl radical * (generated by irradiation of a solution of tri-isobutylborane and di-t-butyl peroxide in cyclopropane[22]) as a function of light intensity. At maximum light intensity the increase in sample temperature was *ca.* 5 °C.

Samples were prepared by using a standard vacuum line and were sealed under vacuum into 4 mm (o.d.) Suprasil tubes and kept in liquid nitrogen until required; they were then repeatedly inverted in a solid $CO_2$–methylated spirits bath until the reagents had dissolved in the solvent (usually cyclopropane).

Spectrum simulation, including the effects of exchange,

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* Analysis of the data given by R. W. Fessenden (*J. Chim. phys.*, 1964, **61**, 1570) gives $T(°C) = 2.21B^2 - 164.62B - 2909.47$, where $B$ is the β-proton hyperfine splitting of the isobutyl radical, in gauss, between −47 and −145 °C. We are grateful to Dr. P. G. Allies for performing the stepwise regression analysis.

[21] (*a*) R. G. Cavell, R. D. Leary, and A. J. Tomlinson, *Inorg. Chem.*, 1972, **11**, 2578; (*b*) R. G. Cavell, D. D. Poulin, K. I. The, and A. J. Tomlinson, *J.C.S. Chem. Comm.*, 1974, 19; (*c*) D. D. Poulin and R. G. Cavell, *Inorg. Chem.*, 1974, **13**, 3012; (*d*) J. W. Gilje, R. W. Braun, and A. H. Cowley, *J.C.S. Chem. Comm.*, 1974, 15; (*e*) K. I. The and R. G. Cavell, *ibid.*, 1975, 279, 716.

[22] A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc.* (*B*), 1971, 1823.

was accomplished by using the program ESREXN obtained from QCPE (program no. 209).

*Materials*.—(a) *Radical sources*. Perfluorodi-t-butyl peroxide,[23] bistrimethylsilyl peroxide,[24] diethyl peroxide,[13] and azomethane [25] were prepared according to literature methods. Di-t-butyl peroxide, trifluoromethyl iodide, perfluoroethyl iodide, and hexamethylditin were obtained commercially and purified before use.

(b) *Phosphorus compounds*. The diethyl fluoroalkyl phosphites were prepared, usually on a 0.05 mol scale, by the following general procedure. An ethereal solution of diethyl chlorophosphite (0.05 mol) was added dropwise during 0.5 h to a stirred, ice-cooled solution of the alcohol (0.05 mol) and triethylamine (0.05 mol) in ether. The mixture was then stirred at room temperature for 1 h, the amine hydrochloride filtered off, the ether removed under reduced pressure, and the residue distilled to yield the product (Table 3).

TABLE 3

Diethyl fluoroalkyl phosphites

| Ester | Formula | B.p. (°C) [mmHg] | Required (%) | | | Found (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | P | C | H | P |
| $(EtO)_2POC(CF_3)_3$ | $C_8H_{10}F_9O_3P$ | 40—41 [8] | 27.0 | 2.8 | 8.7 | 27.1 | 2.8 | |
| $(EtO)_2POC(CF_3)_2(CH_3)$ | $C_8H_{13}F_6O_3P$ | 71—73 [30] | 31.8 | 4.3 | 10.3 | 32.1 | 4.4 | 10.0 |
| $(EtO)_2POC(CF_3)(CH_3)_2$ | $C_8H_{16}F_3O_3P$ | 54—56 [10] | 38.7 | 6.5 | 12.5 | 39.0 | 6.7 | 12.8 |
| $(EtO)_2POCH_2CF_3$ | $C_6H_{12}F_3O_3P$ | 52—53 [10] | 32.8 | 5.5 | 14.1 | 32.3 | 5.3 | |
| $(EtO)_2POCH_2CH_2F$ | $C_6H_{14}FO_3P$ | 64—66 [10] | 39.1 | 7.7 | 16.8 | 39.4 | 7.8 | 16.7 |

The phosphite $(EtO)_2POC(CF_3)_2(CD_3)$ was prepared in a similar manner from the deuteriated alcohol. Trideuteriomethylmagnesium iodide was prepared by the reaction of trideuteriomethyl iodide (25 g, 0.172 mol) with magnesium turnings (4.29 g, 0.178 mol) in dry ether (150 ml). The excess magnesium was filtered off and hexafluoroacetone was bubbled through the solution, maintained at 20 °C and vigorously stirred, until saturation (*ca*. 1.5 h). The mixture was refluxed for a further 1.5 h then cooled, and water (3.1 g, 0.172 mol) was added with stirring during 0.5 h. After filtration the solution was distilled to yield the alcohol $(CD_3)(CF_3)_2COH$ as a complex with ether, b.p. 72 °C, which was converted directly into the phosphite (b.p. 55—57 °C at 9 mmHg).

*Diethoxytrifluoromethylphosphine* was prepared by the reaction of $CF_3PCl_2$ (0.651 g, 3.81 mmol) with ethanol (0.224 g, 10.0 mmol) and $Me_3N$ (0.453 g, 7.69 mmol) in a sealed tube (20 °C; 1 h) which gave, after vacuum fractionation and absorption of the excess of ethanol on phosphorus pentaoxide, $CF_3P(OEt)_2$ (0.400 g, 2.10 mmol). The product released 0.99 mol of $CF_3H$ per mol of phosphine upon alkaline hydrolysis (calc. 1.00 mol). The $^{19}F$ n.m.r. [Brüker Spectrospin HFX instrument at 84.66 MHz; $CCl_3F$ as internal standard (0 p.p.m.)] showed a doublet ($\phi$ 73.4 p.p.m., $J_{FP}$ 83 Hz).

2-*Trifluoromethyl*-1,3,2-*dioxaphospholan*. This was prepared and identified by the literature method.[26] The yield at first was low (*ca*. 10%), but this was increased to 60% by repeatedly heating (60—70 °C) the less volatile fraction, which presumably contained polymeric material, to establish an equilibrium with the cyclic monomer, which was removed by distillation. The product showed a $^{19}F$ n.m.r. doublet ($\phi$ 73.9 p.p.m., $J_{FP}$ 56 Hz), with additional fine structure.

The phosphines $CF_3PH_2$,[27] $(CF_3)_2PH$,[27] $CF_3PCl_2$,[28] $(CF_3)_2PCl$,[28] $(CF_3)_2P{\cdot}P(CF_3)_2$,[28] and $(CF_3)_3P$,[28] and the arsine $(CF_3)_3As$ [29] were prepared according to literature methods.

We thank the S.R.C. for a studentship (to R. W. D.) and for a grant to purchase equipment. We are grateful to Professor A. G. Davies for his interest in this project, and to Dr. D. Griller for carrying out some of the initial experiments on trifluoromethylphosphoranyl radicals.

[6/1738 *Received*, 13*th September*, 1976]

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[25] R. Renaud and L. C. Leitch, *Canad. J. Chem.*, 1954, **32**, 545.

[26] A. B. Burg and J. E. Griffiths, *J. Amer. Chem. Soc.*, 1961, **83**, 4333.

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

[28] F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1565.

[29] G. R. A. Brandt, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1952, 2552.