Dioxabenzofluorophospholes containing more than One Fluorine Atom Bonded to Phosphorus

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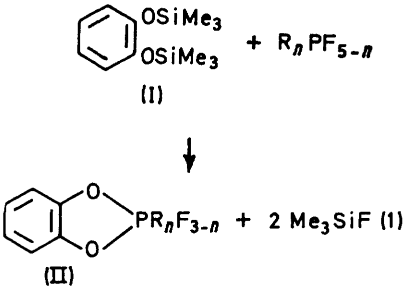
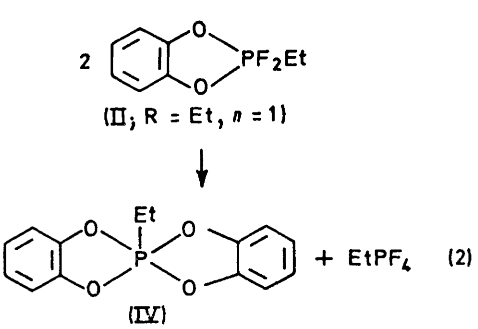
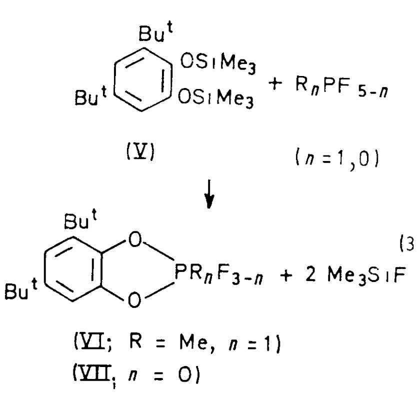
Summary The preparation and n.m.r. spectra of di- and tri-fluorophosphoranes, containing the 2,4-di-t-butylcatechol ring system linked to five-co-ordinate phosphorus, are described.

ATTEMPTS at the preparation of 1,3,2-dioxa-4,5-benzophospholes (II), containing more than one fluorine atom bonded to phosphorus (*i.e.* $n = 0, 1$), by the reaction of (I) with fluorophosphoranes, R_nPF_{5-n}, (equation 1) have not been successful, to date. In the reaction of (I) with PF_5 only the spiro-compound (III) was obtained, while ethyltetrafluorophosphorane and (I) reacted with formation of (II; R = Et, $n = 1$) which, however, was not stable enough to be isolated.[1,2] (II) readily underwent ligand exchange with formation of ethyltetrafluorophosphorane and spirophosphorane (IV) (equation 2).

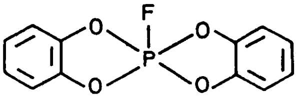




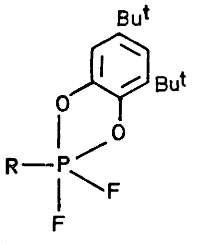
In order possibly to effect and even completely suppress the ligand exchange we have synthesized the new bis-t-butyl-substituted *o*-phenylenedioxybistrimethylsilane (V) and studied its reaction with $MePF_4$ and PF_5 (equation 3).



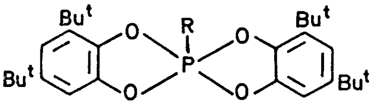
With the former, (VI) was obtained as a stable, distillable liquid. As a by-product the spiro-compound (VIII) was formed. Phosphorus pentafluoride and (V) reacted to give (VII) and the spiro-compound (IX). (VII) is an example of a compound of five-co-ordinate phosphorus in which only the electronegative elements, oxygen and fluorine are



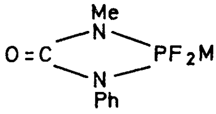
(III)



(VI; R = Me) (VII; R = F)



(VIII; R = Me) (IX; R = F)



(X)

bonded to phosphorus. The compound is obtained as a distillable liquid, fuming strongly in air and undergoing ligand reorganization with formation of PF_5 and (IX).

Assuming that the bis-t-butylcatechol ring bridges one axial and one equatorial position around a central trigonal-bipyramidal phosphorus atom, the structures (VI) and (VII) are suggested for these compounds.

The ^{19}F n.m.r. spectra of (VI) and (VII) show only one fluorine atom environment at room temperature, and the δ_F and J_{P-F} values observed are intermediate between "normal" axial and equatorial δ_F and J_{P-F}.[3] On cooling the sample to −88° the ABX spectrum shown in the Figure was observed in the ^{19}F resonance of (VI). The close similarity of δ_F and J_{P-F} for both fluorine atoms in this spectrum indicates that they are both still exchanging between axial and equatorial sites. The non-equivalence may then be explained by a rapid exchange occurring between structures (A) and (B). Equivalence of the two fluorine atoms is only achieved by exchange processes passing through structure (C), which is expected to be of higher energy owing to the more electropositive R group being in an axial position. A similar effect is observed for the related compound (X) where the non-equivalence of the two nitrogen atoms leads to non-equivalence of the two fluorine atoms in the low temperature n.m.r. spectra.[4]

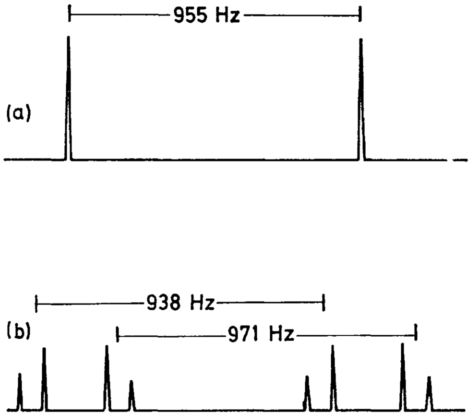
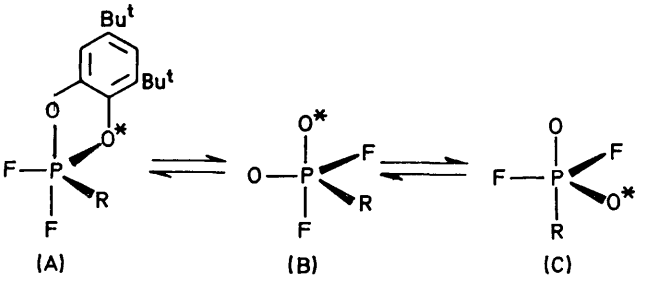


FIGURE. ^{19}F *n.m.r. spectrum of* (VI; R = Me) *at* 32° (a) *and at* −88° (b) (*toluene solvent.*)



In the case of (VII) structure (C) will be of the same energy as (A) and (B), so that rapid exchange between all three structures is expected and, in fact, the three fluorine atoms are equivalent at room temperature.

As a consequence of unsymmetric substitution of the catechol rings, two isomers of the spiro-compounds (VIII) and (IX) are to be expected. Different δ_{Me} and δ_F values are indeed observed for (VIII) and (IX). No further splitting of the Bu^t resonance is observed in the 60 MHz ^1H spectra, however. The n.m.r. parameters are listed in the Table.

N.m.r. parameters of 2,4-*di-t-butylcatechol phosphoranes*

Compound	δ_F[a,b]	J_{P-F}[c]	δ_P[b,d]	δ_H[b,e,f]	δ_H[b,f,g]	$^2J_{H-P}$[c]	$^3J_{H-F}$[c]
(VI)	39·0	957	12·1	−1·93	−1·36 −1·27	19·5	6·5
(VII)	61·1	915	51·7		−1·46 −1·36		
(VIII)			−3·0	−1·93 −1·81	−1·33 −1·10	18·0 18·0	
(IX)	68·9 70·1	992 994	25·9		−1·48 −1·36		

[a] Internal CCl_3F reference. [b] In p.p.m. [c] In Hz. [d] External 85% H_3PO_4 reference. [e] δ_H of Me–P. [f] Internal $SiMe_4$ reference. [g] δ_H of Me_3C.

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