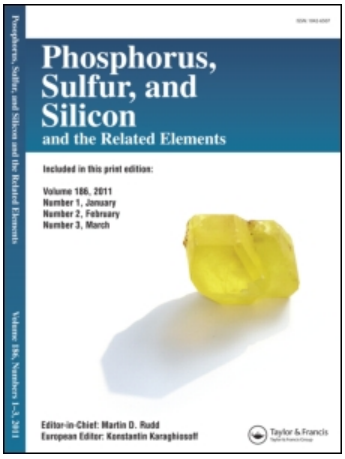

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On The Preparation And Pseudorotation Of Certain Monocyclic Pentaoxyphosphoranes

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ON THE PREPARATION AND PSEUDOROTATION OF CERTAIN MONOCYCLIC PENTAOXYPHOSPHORANES*

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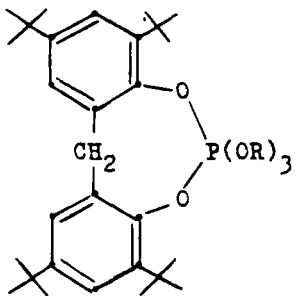
The S-bridged pentaoxyphosphorane *2a* has been prepared for the first time and its ground-state structure studied on the time scale of NMR (^1H, ^{19}F, ^{31}P, and ^{13}C) spectroscopic measurements. Compound *2a* was found to show significant barriers to intramolecular ligand rearrangement (pseudorotation). A comparative study on non-bridged pentaoxyphosphoranes of type *14* was also undertaken.

The ground-state structure of pentaoxyphosphoranes has been extensively studied by electron diffraction, X-ray diffraction, microwave and vibrational spectroscopy.[1] To the best of our knowledge, however, relatively limited attention[2] has been devoted to the application of NMR spectroscopy as a tool for studying the ground-state structure and ligand apicophilicities of monocyclic pentaoxyphosphoranes. This may be ascribed to the low ΔG^* necessary to induce intramolecular ligand rearrangement (pseudorotation) in these pentaoxyphosphoranes. In a recent study[3] on the slowing of pseudorotation on the NMR time scale for caged polycyclic pentaoxyphosphoranes, we have shown that compounds **1** exhibit significant barriers to intramolecular ligand reorganization.



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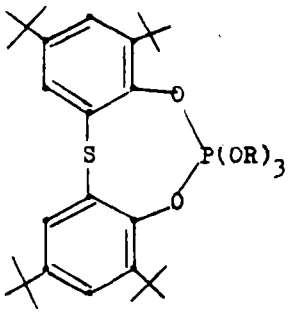


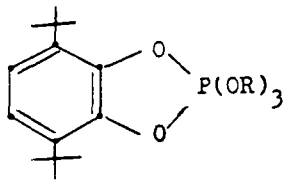
2

a, R = CH_2CF_3
b, R = CH_2CH_3

It appeared of interest to extend this investigation to include phosphoranes of type **2** in order to gain knowledge about the effect of substitution of sulfur for the methylene, as a bridging group, on the pseudorotation of the molecule. The introduction of electronegative ligands, e.g., the $-CH_2CF_3$ group (cf. **2a**) is expected

*Dedicated to Professor Dr. M. M. Sidky on the occasion of his 56th birthday.

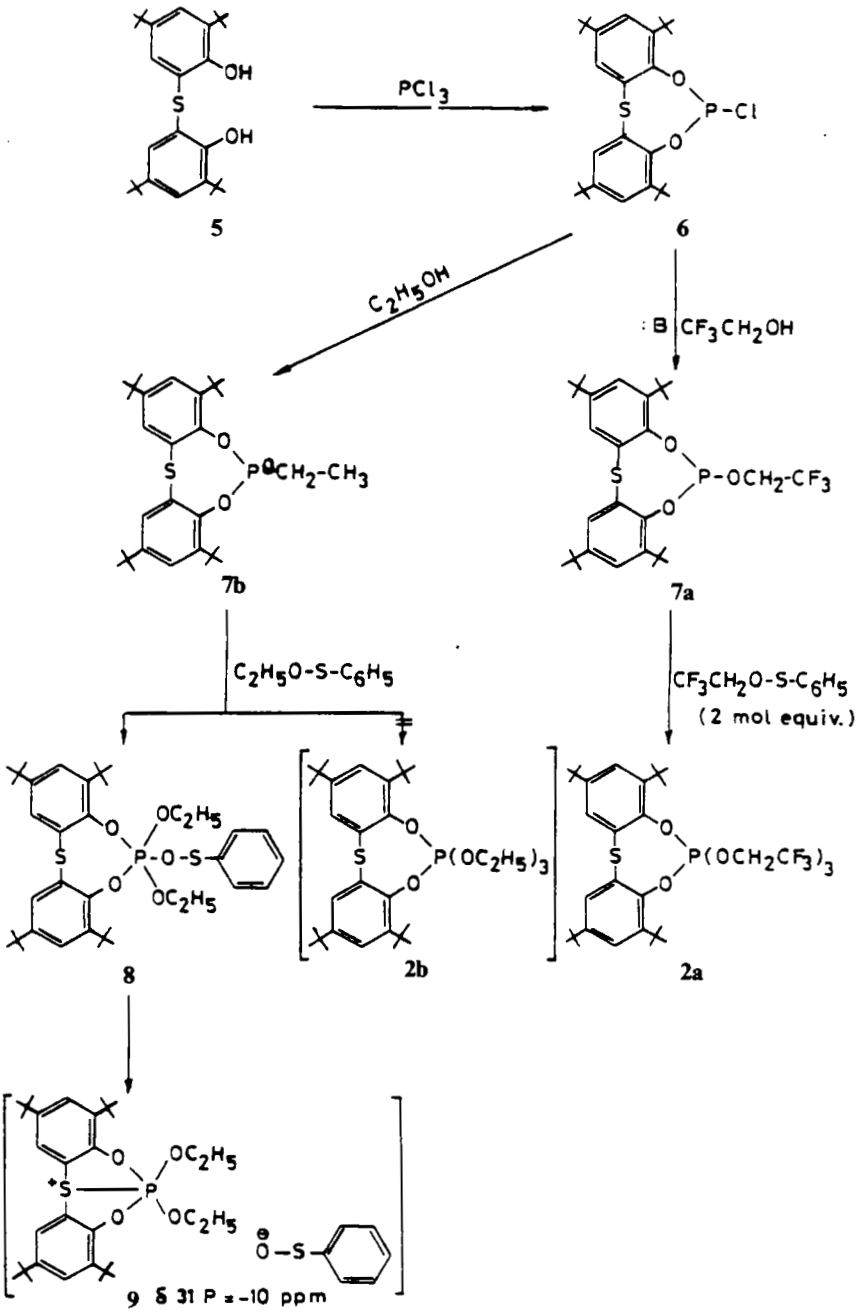
to impose a certain stability in the oxyphosphorane ring[4,5]. A comparative study on non-bridged pentaoxyphosphoranes of type **14** (cf. Scheme 2) was also undertaken to manifest the role displayed by the *tert*-butyl groups on the pseudorotation rates.



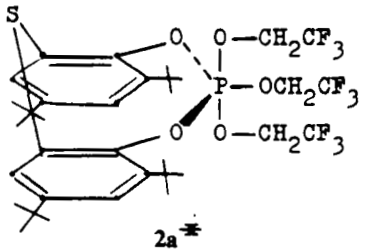
14 a, R= CH_3 ; **b**, R= $CH(CF_3)_2$; **c**, R= CH_2CF_3

RESULTS AND DISCUSSION

The *S*-bridged pentaoxyphosphorane **2a** was prepared for the first time (Scheme 1) by the reaction of 2,2′-thiobis-(4,6-di-*tert*-butylphenol) **5** with PCl_3 to afford the phosphorochloridite **6** which shows a marked stability towards atmospheric moisture, presumably, due to the steric retardation induced by the *tert*-butyl group in the ortho position to the —O—P-linkage.[6-8] Treatment of **6** with 2,2,2-trifluoroethanol gives the respective trioxophosphorane **7a** which yields **2a** upon reaction with 2,2,2-trifluoroethoxybenzenesulfenate. Attempted preparation of the pentaoxyphosphorane analogue **2b** by a similar route was, however, unsuccessful even after the reaction of the trioxophosphorane **7b** with two mole-equivalents of ethoxybenzenesulfenate in CH_2Cl_2 at $-78°C$. The reaction indicated only the formation of a phosphate ($\delta^{31}P$ NMR = -10 ppm). This finding strongly suggests that the trans-annular sulfur atom interacts with the mixed thio-oxyphosphorane **8**, initially formed, resulting thus in decomposition to a phosphate structure like **9** (Scheme 1). The *S*-bridged pentaoxyphosphorane **2a** is quite unstable and its spectral data vary considerably according to the sample's history. The ^{31}P NMR spectrum of a freshly prepared sample of **2a** had a resonance at δ − 69.86 ppm, which is typical of a pentaoxyphosphorane structure.[1a] The ^{19}F NMR spectrum of **2a** at 26°C, showed two triplets (2:1 integration-ratio) which lends additional support to the assigned structure. The variable-temperature ^{19}F NMR spectra of **2a** showed that it was possible to slow the pseudorotation only at $-65°C$ (the coalescence temperature). This was indicated by the appearance of three triplets (1:1:1 integration-ratio) at $\delta = -74.24$, $\delta = -74.56$ and $\delta = -74.85$ ppm, respectively; denoting the presence of three non-equivalent fluorine atoms. The activation energy (ΔG^*), required to render the three CF_3—CH_2— groups equivalent to each other, was too low to be measured. Measuring the ^{19}F NMR spectrum of **2a** at 110°C, resulted only in recording an ill-defined triplet at $\delta = -74.78$ ppm. This finding is also consistent with rapid ligand reorganization. It seems, as a requisite for the appearance of three non-equivalent fluorine-atom resonances in the spectrum of **2a** to occur, that the eight-membered ring should be non-planar in order to allow for the non-equivalency of the apical trifluoroethoxy groups. This would be the case if **2a** exists in a trigonal bipyramidal (TBP) structure like **2a*** wherein the two electronegative trifluoro-ethoxy ligands are in apical positions. Other alternative

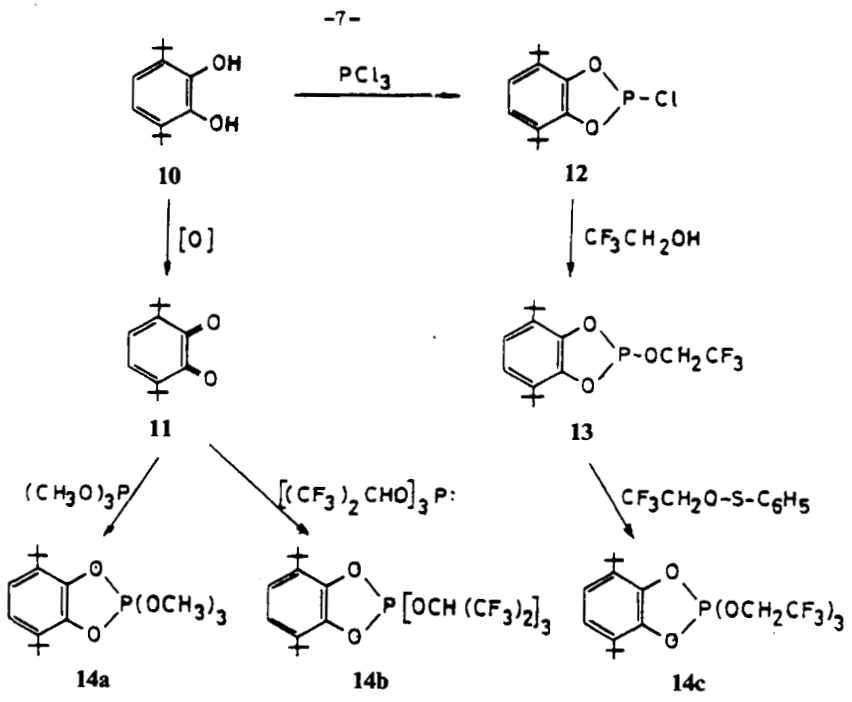


SCHEME 1



2a

square (SP) or rectangular (RP) structures, on the other hand, would not accomodate the aforementioned spectral data. Variable temperature ^{1}H NMR and ^{13}C NMR spectra for **2a** are also in good accord with the above arguments. Thus, the ^{1}H NMR spectrum of **2a** at $-65°C$ disclosed the presence of three pairs of doublets centered at δ4.10, 4.42 and 4.55 due to the non-equivalent trifluoroethoxy-CH_2 protons. This observation recalls the appearance of three triplets (1:1:1 integration ratio) in the ^{19}F NMR spectrum of **2a** at $-65°C$; attributable to the presence of three non-equivalent fluorine atoms in the molecule (*vide-supra*). At 110°C, the ^{1}H NMR spectrum of **2a** showed only a doublet of quartets assignable to three equivalent trifluoroethoxy-CH_2 protons. The observed coupling between phosphorus and the $-CH_2$ protons in **2a** at high temperature (110°C) shows that the ligand rearrangement should be intramolecular in nature due to fluxioning of the molecule and does not



SCHEME 2

TABLE I*

Cpd.	T°C	^{31}P	^{19}P	^{1}H				
7A	26[A]	130.3	−74.74(*T*) J_{FCCH} = 5.1 J_{FCCOP} = 0	1.28(S)	1.45(S)	3.87(*d* of *q*) J_{HCCF} = 4.5 J_{HCOP} = 1.2		7.07–7.2
				18 H	18 H	2 H		4 H
				$C(CH_3)_3$	$C(CH_3)_3$	$-O-CH_2-$		Arom.
7b	26[a]	129		1.25(s)	1.42(s)	1.46(*c*)	3.9(*d* of *q*) J_{HCCH} = 4.8 J_{HCOP} = 4.8	6.9–7.2
				18 H	18 H	3 H	2 H	4 H
				$C(CH_3)_3$	$C(CH_3)_3$	CH_3CH_2	$-O-CH_2-$	Arom.
2a	26[b]	−69.86	−75(*d* of *t*) J_{FCCH} = 8.1 J_{FCCOP} = 1.2 and −75.8(*d* of *t*) J_{FCCH} = 8.1 J_{FCCOP} = 1.3	1.28(s)	1.42(s)	4.20(*d* of *q*) J_{HCCF} = 4.8 J_{HCOP} = 1.4	4.41(*d* of *q*) J_{HCCF} = 4.8 J_{HCOP} = 1.4	7.0–7.25
				18 H	18 H	2 H	4 H	4 H
				$C(CH_3)_3$	$C(CH_3)_3$	$-O-CH_2-$	$-O-CH_2-$	Arom.
	−65[b]		−74.24(*t*) J_{FCCH} = 8.1 and −74.56(*t*) J_{FCCH} = 8.1 and	1.31(s)	1.49(s)	4.10(*d* of *q*) J_{HCCF} = 4.8 J_{HCOP} = 1.4	4.42(*d* of *q*) J_{HCCF} = 4.8 J_{HCOP} = 1.4	4.55(*d* of *q*) J_{HCCF} = 4.8 J_{HCOP} = 1.4
			−74.85(*t*) J_{FCCH} = 8.1	18 H $C(CH_3)_3$	18 H $C(CH_3)_3$	2 H $-O-CH_2-$	2 H $-O-CH_2-$	2 H $-O-CH_2-$
	110[b]		−74.78(*t*) J_{FCCH} = 8.1	1.34(s)	1.52(s)	4.45(*d* of *q*) J_{HCCF} = 4.8		7.22–7.68
				18 H	18 H	6 H		4 H
				$C(CH_3)_3$	$C(CH_3)_3$	$-O-CH_2-CH_3$	$-O-CH_2-$	Arom.
2b	26[b]	−10 and −12		1.25(s)	1.40(s)	1.48(*c*)	4.4(*d* of *q*) J_{HCCH} = 4.8 J_{HCOP} = 4.8	6.9–7.2
				18 H	18 H	6 H	4 H	
				$C(CH_3)_3$	$C(CH_3)_3$	CH_3	$-O-CH_2-$	Arom.
13	26[a]	125.23	−74.1(*d* of *t*) J_{FCCH} = 4.1 J_{FCCOP} = 1.95	1.4(s)	3.8(*d* of *q*) J_{HCCF} = 8.4 J_{HCOP} = 4.6	7.1(s)		
				18 H	4 H	2 H		
				$C(CH_3)_3$	$-O-CH_2-$	Arom.		
14a	26[b]	−47.73		1.4(s)	3.8(*d*) J_{HCOP} = 14	6.8(s)		
				18 H	9 H	2 H		
				$C(CH_3)_3$	$-O-CH_3$	Arom.		
14b	26[b]	−58.25	−75.58(*d*) J_{FCCH} = 6.7 J_{FCOP} = 0	1.3(s)	4.6(*d* of *sept.*) J_{HCCF} = 4.5 J_{HCOP} = 1.5	6.8(s)		
				18 H	3 H	2 H		
				$C(CH_3)_3$	$CH(CF_3)_2$	Arom.		
14c	26[b]	−51.93	−75.96(*d* of *t*) J_{FCCH} = 8.6 J_{FCCOP} = 3.1	1.4(s)	4.4(*d* of *q*) J_{HCCF} = 8.6 J_{HCOP} = 4.0	7.0(s)		
				18 H	6 H	2 H		
				$C(CH_3)_3$	$-O-CH_2-$	Arom.		

*See experimental for details of NMR experiments.
[a] The solvent is $CDCl_3$.
[b] The solvent is CD_2Cl_2
[c] The hydrogens of the CH_3 group are partially obscared by those of the *t*-butyl groups.

TABLE II*

^{13}C NMR Spectral Data

Cpd./C[a]	1	2	3	4	5	6	7	8	9	10	11	12
7a[b]	29.5(*d*) J = 1.9	31.6(*s*)	34.3(*s*)	36.02(*d*) J = 7.2	60.4(*d* of *q*) J = 36.3 J = 2.1	122.5(*d* of *q*) J = 224.2 J = 12.3	105.3(*d*) J = 11.1	123.2(*d*) J = 0.48	135.8(*d*) J = 3.6	144(*d*) J = 2.1	145.2(*d*) J = 5.6	148(*d*) J = 1.0
7b[b]	31.3(*d*) J = 3.3	32.4(*s*)	34.6(*s*)	35.2(*d*) J = 9.3	58.7(*d*) J = 3.4	17.6(*d*) J = 2.5	106.1(*d*) J = 9.5	123.8(*d*) J = 0.4	135.2(*d*) J = 3.6	142(*d*) J = 1.5	145(*d*) J = 4.8	147.1(*d*) J = 0.9
2a[c]	29.4(*d*) J = 2.2	31.8(*s*)	34.3(*s*)	35.8(*d*) J = 9.5	64.1(*d* of *q*) J = 36.7 J = 2.4	123.9(*d* of *q*) J = 254.8 J = 12.5	124.2(*d*) J = 14.2	135.6(*d*) J = 5.1	136.9(*d*) J = 5.4	144.2(*d*) J = 2.8	146(*d*) J = 7.2	148.8(*d*) J = 1.5
13[b]	29.0(*s*)	34.4(*s*)	120.3(*d*) J = 0.5	123.3(*d*) J = 5.2	60.8(*d* of *q*) J = 26.9 J = 1.6	122.9(*d* of *q*) J = 273 J = 1.2	134.4(*d*) J = 0.7					
14a[c]	30.1(*s*)	34.1(*s*)	117.0(*d*) J = 0.7	120.0(*d*) J = 5.6	56.1(*d*) J = 10.6		131.2(*d*) J = 0.65					
14b[c]	30.9(*s*)	34.5(*s*)	119.9(*d*) J = 1.0	124.8(*d*) J = 6.3	74.2 (*d* of *sept.*) J = 26.2 J = 11.5	127.9(*d* of *q*) J = 277.3 J = 11.5	135.3(*d*) J = 1.3					
14c[c]	32.8(*s*)	34.8(*s*)	119.3(*d*) J = 1.3	125.2(*d*) J = 5.7	68.4(*d* of *q*) J = 28.9 J = 1.6	129.1(*d* of *q*) J = 277.3 J = 11.64	131.8(*d*) J = 1.3					

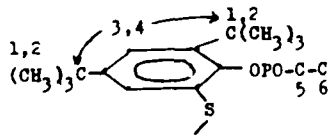


Figure I

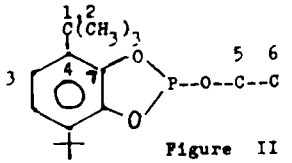
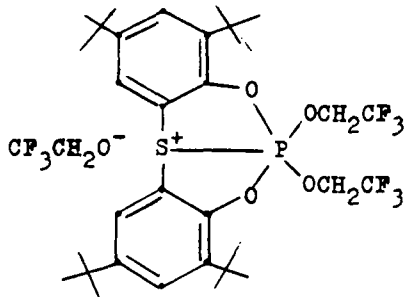


Figure II

*See experimental for details of NMR experiments. Since all spectra are proton decoupled, the coupling constants listed reflect coupling to fluorine and phosphorus. [a]The numbering system is as in Figures I and II. [b]The solvent is $CDCl_3$. [c]The solvent is CD_2Cl_2.

involve any ionization processes.[9] However, such coupling can be reasonably explained in terms of rapid ring inversion above the coalescence temperature.[10]

The relative unstability of compound **2a** can be attributed to the interaction between sulfur and phosphorus which may result in the contribution of a form like **15** to the ground state of the molecule. The well-established interaction of



15

nucleophiles with pentacoordinate phosphorus[11] is in favour of this conclusion. The ^{1}H NMR spectrum of compound **2b** was also consistent with the assigned structure. It showed the *tert*-butyl-CH_3 protons as two singlets at δ1.40 (18H) and 1.85 (18H). The ethoxy-CH_2 protons (6H) appeared as a doublet of quartets centered at δ4.4 while the ethoxy-CH_3 protons (9H) exhibited a triplet at δ1.48 which was partially obscared with the signals due to the tert-butyl groups. The Multiplet at δ6.90–7.20 was due to the aromatics (4H).

Further, quinone **11** reacted with trimethylphosphite, tris-(1,1,1,3,3,3-hexafluoro-iso-propyl) phosphite to yield the pentaoxyphosphorane adducts **14a** and **14b**, respectively. On the other hand, the pentaoxyphosphorane **14c** could be prepared by allowing 2,2,2-trifluoroethyl-3,6-di-tert-butyl-1,2-benzoquinolene phosphite **13** with trifluorobenzenesulfenate (cf. Scheme 2). Spectral investigations for compounds **14a–c** were also performed and the data were collected in Tables I and II. In no case, however, did variable temperature NMR studies show appreciable slowing of pseudorotation. The ^{31}P NMR spectrum of a freshly prepared sample of **14a** taken as a representative example, had a resonance at $\delta = -47.73$ ppm, which is compatible with the pentaoxyphosphorane structure. Its ^{1}H NMR spectrum showed the *tert*-butyl protons as a singlet (18H) at $\delta = 1.30$ while the —OCH_3 protons attached to phosphorus (9 H) appeared as a doublet ($J_{HP} = 14$ Hz) at $\delta = 3.80$. The aromatic protons (2 H) appeared as a singlet at $\delta = 6.80$.

The results of these investigations clearly support the concept of steric hindrance as a means for decreasing pseudorotation rates in pentaoxyphosphoranes. In addition, the presence of a bridging group (like sulfur in **2a**) as an important requisite to cause pseudorotation, is stressed.

EXPERIMENTAL

All melting points were determined in open capillary tubes on a Mel-Temp. apparatus and are uncorrected. The reactions were carried out in flame-dried apparatus under nitrogen atmosphere. The ^{1}H NMR spectra were recorded on a Varian Model T-60 and FT-80 spectrometers. The chemical shifts are

reported in ppm relative to TMS. The ^{19}F, ^{31}P and ^{13}C NMR spectra were taken on a Varian Spectrometer equipped with a 5 or 10 mm variable temperature broad-band probe. ^{31}P chemical shifts are reported in ppm vs 85% H_3PO_4 (external). The ^{19}F chemical shifts are reported in ppm relative to CCl_3F. Moisture and Oxygen should be avoided while preparing the 1:1 adducts.

Materials and reagents were purchased from Aldrich Company.

Preparation of 2,4,8,10-Tetra-tert-Butyl-6(2,2,2-Trifluoethoxy)-Thiobiphenylene Phosphite (**7a**). A solution of PCl_3 (13.37 g; 0.1 mol) in toluene (100 ml) was cooled to 5°C then treated with a mixture of 2,2'-thiobis(4,6-di-tert-butylphenol)[12] (44.20 g; 0.10 mol) and triethylamine (20.24 g; 0.20 mol) in toluene (80 ml). The reaction mixture was kept at room temperature under good stirring for 5 hr., to ensure complete disappearance of the phenol (TLC), then cooled to 5°C. The reactants were treated with a mixture of dry 2,2,2-trifluoroethanol (10 g; 0.1 mol) and pyridine (7.91 g; 0.1 mol) and the mixture stirred for 20 hr., at room temperature then filtered to remove triethylamine hydrochloride. The filtrate was freed from the solvents *in vacuo* and the residue was distilled under reduced pressure to give **7a** as a colourless viscous oil, b.p. 110–115/0.05 mm (yield: 20 g; 40%). Anal. Calcd. for $C_{30}H_{42}F_3O_3PS$: C, 63.18; H, 7.40. Found: C, 63.09; H, 7.25.

Similarly, 2,4,8,10-tetra-*tert*-butyl-6-ethoxy-thiobiphenylene phosphite (**7b**) was prepared in 45% yield, when ethanol was used in place of 2,2,2-trifluoroethanol in the above-described procedure. Compound **7b** was obtained as a colourless viscous liquid, b.p. 120–125/0.05 mm Anal. Calcd. for $C_{30}H_{45}O_3PS$: C, 69.74; H, 8.77. Found: C, 70.20; H, 8.26.

Preparation of The Pentaoxyphosphorane **2a**. A solution of 2,2,2-trifluoroethyl benzenesulfenate[13] (0.7 g; 0.0036 mol) in CH_2Cl_2-d_2 (2 ml) was added to a stirred solution of **7a** (1 g; 0.0018 mol) in the same solvent (5 ml) at −78°C. The reaction mixture was allowed to warm till room temperature and further stirred for an hour, then recooled to −70°C and filtered (filtrate **A**). Filtrate **A** which contained **2a** was taken immediately, and subjected to different spectral measurements. When the volatile materials in filtrate **A** were evaporated at 20°C under reduced pressure; it gave a pale-yellow oil (decomposable upon attempted purification by molecular distillation at 50°C/0.05 mm).

Reaction of **7b** *with Ethyl Benzenesulfenate. Attempted Preparation of the Pentaoxyphosphorane* **2b**. A solution of ethyl benzenesulfenate (0.6 g, 0.0038 mol or 0.3 g; 0.0019 mol) in CH_2Cl_2-d_2 (2 ml) was added to a stirred solution of **7b** (1 g; 0.0018 mol) in the same solvent (4 ml) at −78°C. The reaction mixture was allowed to warm till room temp., and further stirred for an hour, then recooled to −70°C and filtered. Spectral analyses showed that phosphate **9** (and not phosphorane **2b**) was present in the filtrate, almost exclusively ($\delta^{31}P$ NMR: −10 ppm).

Preparation of 3,6-Di-tert-Butylcatechol **10**. The procedure reported[14] by I. S. Belostoskaya *et al.* for the preparation of 3,6-di-*tert*-butylcatechol was modified as follows:

A pressure-reactor was charged with a mixture of catechol (40 g; 0.6 mol), titanium catecholate[14] (3 g) and iso-butylene (80 ml, 1.2 mol) in xylene (100 ml) then heated at 120–130°C for 6 hr. The volatile materials were evapoarated, *in a vacuo*, and the residue distilled under reduced pressure to give 3,6-di-*tert*-butylcatechol (72 g; 95%); b.p. 160/0.1 mm. The product was contaminated with *ca.* 4% of 3,5-di-*tert*-butylcatechol. 3,6-Di-*tert*-butylcatechol can be obtained pure after crystallization twice from hexane, m.p. 96°C.

3,6-Di-tert-Butyl-1,2-Benzoquinone **11**. A mixture of nitrogen oxides (5 ml) was bubbled into a stirred solution of 3,6-di-tert-butylcatechol (20 g; 96% purity) in CCl_4 (100 ml) and stirring was continued for 15 min. The precipitated material was filtered off and recrystallized twice from cyclohexane to give 3,6-di-*tert*-butyl-1,2-benzoquinone (16.5 g; 82%) as dark brown needles, m.p. 198–200°C (reported[15] m.p. 196°C).

Preparation of 3,6-Di-tert-Butyl-1,2-Benzoquinonelene Phosphorochloridite **12**. 3,6-Di-*tert*-butylcatechol (10 g; 0.04 mol) was treated with PCl_3 (26.2 g; 0.1 mol) and the mixture heated at 100–110°C (bath temperature) till evolution of HCl gas ceased. Excess of PCl_3 was distilled off *in vacuo*, and the residue distilled under reduced pressure to give phosphorochloridite as a colourless liquid (11.5 g; 87%), b.p. 100–103°C/0.1 mm.

2,2,2-Trifluoroethyl-3,6-Di-tert-Butyl-1,2-Benzoquinolene Phosphite **13**. A solution of the phosphorochloridite (10 g; 0.0035 mol) in dry ether (50 ml) was added dropwise within 30 minutes to a mixture of pyridine (2.7 g; 0.0035 mol) and 2,2,2-trifluoroethanol (3.5 g; 0.0035 mol) in dry ether (50 ml) at −50°C. The mixture was allowed to warm slowly to room temperature under good stirring for 2 hr. Pyridine hydrochloride was filtered off and the ether evaporated from the filtrate, *in vacuo*. The residue was then

distilled under reduced pressure to give the phosphite ester **13** as a viscous liquid (7.9 g; 65%), b.p. 120–122°C/0.2 mm. Anal. Calcd. for $C_{16}H_{22}F_3O_3P$: C, 55.06; H, 6.30. Found: C, 54.75; H, 6.08.

Preparation of Pentaoxyphosphorane **14a**. To a solution of quinone **11** (0.2 g, 0.001 mol) in CH_2Cl_2-d_2 was added a solution of trimethyl phosphite (0.13 g; 0.0012 mol) in the same solvent (2 ml) at −70°C. The reaction mixture was allowed to warm slowly to room temperature and further stirred for one hr. The volatile materials were evaporated at 20°C, under reduced pressure (0.05 mm) and the residual crude phosphorane **14a** was dissolved in $CDCl_3$ (4 ml) for running the spectral measurements.

Preparation of Pentaoxyphosphorane **14b**. A solution of tris(1,1,1,3,3,3-hexafluoro-iso-propyl) phosphite[16] (0.5 g; 0.001 mol) in CH_2Cl_2-d_2 (1 ml) was added to a 10 ml NMR-tube cooled at −70°C and containing quinone **11** (0.2 g; 0.001 mol) dissolved in the same solvent (4 ml). The reaction mixture was allowed to warm till room temperature within 3 hr., and subjected to different spectral measurements after standing for 1 hr.

Preparation of Pentaoxyphosphorane **14c**. To a solution of phosphite **13** (3.5 g; 0.01 mol) in CH_2Cl_2-d_2 (10 ml) cooled to −70°C, was added a solution of 2,2,2-trifluoroethyl benzenesulfenate (5.5g; 0.02 mol). The reaction mixture was allowed to warm till room temperature, then recooled to −70°C and filtered. The volatile materials were evapoarated at 20°C under reduced pressure (up to 0.05 mm). The residual crude phosphorane **14c** was pure enough for running various spectral measurements.

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