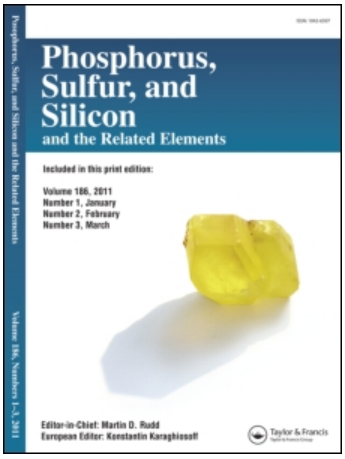

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THE REACTION OF ALKYL PHOSPHITES WITH 3,5-DI-TERT-BUTYL-1,2-BENZOQUINONE. VARIABLE TEMPERATURE NMR STUDIES ON NEW PENTAOXYPHOSPHORANES

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THE REACTION OF ALKYL PHOSPHITES WITH 3,5-DI-TERT-BUTYL-1,2-BENZOQUINONE. VARIABLE TEMPERATURE NMR STUDIES ON NEW PENTAOXYPHOSPHORANES

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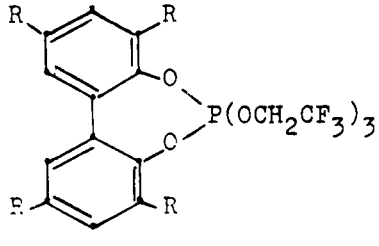
3,5-Di-tert-butyl-1,2-benzoquinone (**5**) reacts with trialkyl phosphites (**6**) to give the respective pentaoxyphosphoranes **7**. On the other hand, the reaction of quinone **5** with dialkyl phosphites affords the phosphonate adducts **13**. Analytical and spectroscopic (^1H, ^{31}P, ^{19}F and ^{13}C NMR) results are in accord with the given structures. The ground state structure of pentaoxyphosphoranes **7** was also studied in the light of NMR time scale spectroscopic results.

INTRODUCTION

The electronic and steric factors on cyclic phosphorane structures and their effect on intramolecular ligand rearrangement (pseudorotation) were the themes of a number of recent studies.[1-5] The first models of inhibition of pseudorotation in monocyclic pentaoxyphosphoranes on the NMR time scale were introduced by Denney *et al.*,[4] who attributed the slow down of pseudorotation in oxyphosphoranes of type **1** to the steric effect induced by the tert-butyl groups since no change was observed in the



1. R= $C(CH_3)_3$
2. R= H

variable temperature ^{19}F NMR spectra of the non-substituted analogue **2**, down to $-55°C$. Moreover, we have shown[5] that similar spectroscopic measurements resulted in absence of any appreciable barriers to pseudorotation in the monocyclic

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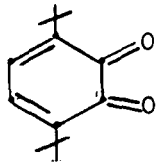

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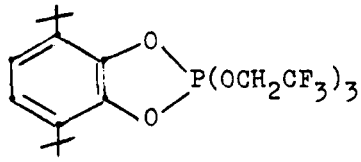

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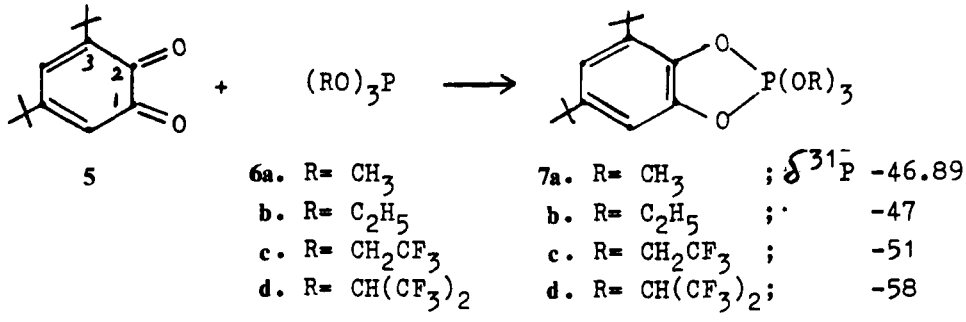
pentaoxyphosphorane **4** which is derived from the symmetrically hindered 3,6-ditert-butyl-1,2-benzoquinone (**3**). This study is now extended to include new pentaoxyphosphoranes of type **7**, which are derived from the asymmetrically hindered 3,5-di-tert-butyl-1,2-benzoquinone (**5**), in order to gain more knowledge about the factors affecting pseudorotation in these monocyclic pentaoxyphosphorane systems.

In order to determine whether nucleophiles other than trialkyl phosphites (**6**) would also attack quinone **5**, preferentially, at the dioxo-system, we have studied its reaction with dialkyl phosphites (**12**).



5

6a. R= CH_3
b. R= C_2H_5
c. R= CH_2CF_3
d. R= $CH(CF_3)_2$

7a. R= CH_3 ; $\delta^{31}P$ -46.89
b. R= C_2H_5 ; -47
c. R= CH_2CF_3 ; -51
d. R= $CH(CF_3)_2$; -58

RESULTS AND DISCUSSION

The new oxyphosphoranes **7a–d** are obtained almost exclusively and in a high yield by reacting 3,5-di-tert-butyl-1,2-benzoquinone (**5**) with trimethyl, triethyl, 2,2,2-trifluoroethyl and 1,1,1,3,3,3-hexafluoroisopropyl phosphites, respectively, in CH_2Cl_2 at $-50°C$. Compounds **7** are moderately stable and can be obtained in a pure form. The reasons for the assigned pentaoxyphosphorane structure **7** are: (a) Correct elemental analyses and compatible ^{31}P, ^{1}H, ^{19}F and ^{13}C NMR data were obtained for all adducts (cf. Tables I, II, III). (b) Compounds **7a–d** show upfield ^{31}P NMR chemical shifts, relative to 85% H_3PO_4; that of **7c** is at -51 ppm which is in a good accordance with a ring pentaoxyphosphorane structure.[6]

In order to study the nature of pseudorotation in adducts **7**, we have examined the variable temperature ^{19}F NMR spectra of compound **7c** as a representative example. Presence of the electronegative $—CH_2CF_3$ ligand in the latter compound is expected to impose certain stability in the oxyphosphorane ring.[7,8] At ambient temperature, the ^{19}F NMR spectrum of **7c** showed one doublet of triplets centered at δ -75

TABLE 1

Comp.	Yield %	M.P.° C	Mol. Formula (Mol. Wt.)	Analysis (Calcd./Found) C	H	P	M^+ (m/e^+)	IR_{-1} cm		
7a	90	65[a]	$C_{17}H_{29}O_5P$	59.28	8.49	8.99				
			344.39	58.87	8.31	8.69	344			
b	82	58[a]	$C_{20}H_{35}O_5P$	62.15	9.13	8.02				
			386.48	62.01	9.25	8.34	386			
c	75	77[a]	$C_{20}H_{26}F_9O_5P$	43.80	4.78	5.65				
			548.40	43.77	4.65	5.47	548			
d	56	60[a]	$C_{23}H_{23}F_{18}O_5P$	34.98	3.16	4.23				
			732.41	34.45	3.05	4.37				
13a	90	87[b]	$C_{16}H_{27}O_5P$	58.17	8.23	9.34		3550	1220	1035
			330.37	57.88	8.07	9.21	330	OH	P=O	P—O—CH_3
b	90	75[b]	$C_{18}H_{31}O_5P$	60.32	8.72	8.64		3530	1245	1040
			358.42	60.01	8.56	8.91	358	OH	P=O	P—O—CH_2
c	80	56[b]	$C_{20}H_{35}O_5P$	62.15	9.13	8.02		3500	1230	1010
			386.48	62.70	9.01	8.27	386	OH	P=O	P—O—CH

[a] Solvent of crystallization is pentane.
[b] Solvent of crystallization is light petroleum.

TABLE 2[a]

Compound	T°C	^{31}P	^{19}F		^1H				
7a	24[b]	−46.89			1.3(s)	1.6(s)	3.8(d)	6.23(d of d)	6.99(d)
							J_{HP} = 13.5	J_{HP} = 8.0	J_{HH} = 4.0
								J_{HH} = 4.0	
					9 H	9 H	9 H	1 H	1 H
					$C(CH_3)_3$	$C(CH_3)_3$	—O—CH_3	arom.	arom.
7b	24[b]	−47.0		[d]	1.25(s)	1.42(s)	3.9(d of q)	6.23(d of d)	6.99(d)
							J_{HP} = 11.5	J_{HP} = 8.0	J_{HH} = 4.0
							J_{HH} = 4.0	J_{HH} = 4.0	
				9 H	9 H	9 H	6 H	1 H	1 H
				CH_3	$C(CH_3)_3$	$C(CH_3)_3$	—O—CH_2	arom.	arom.
7c	24[c]	−51.0	−75(d of t)		1.28(s)	1.45(s)	4.45(d of q)	6.62(d of d)	7.2(d)
			J_{FCCH} = 8.1				J_{HF} = 9.0	J_{HP} = 8.0	J_{HH} = 4.0
			J_{FCOP} = 0.4				J_{HP} = 4.2	J_{HH} = 4.3	
					9 H	9 H	6 H	1 H	1 H
					$C(CH_3)_3$	$C(CH_3)_3$	—O—CH_2	arom.	arom.
	−93[c]		[e]						
7d	24[c]	−58.0	−74.0(d)		1.1(s)	1.3(s)	5.2(d of sept.)	6.4(d of d)	7.3(d)
			J_{FCCH} = 5.1				J_{HF} = 8.9	J_{HP} = 8.0	J_{HH} = 4.0
			J_{FP} = 0				J_{HP} = 4.8	J_{HH} = 4.0	
					9 H	9 H	3 H	1 H	1 H
					$C(CH_3)_3$	$C(CH_3)_3$	—O—CH	arom.	arom.
13a	24[b]	29.84		1.2(s)	1.34(s)	3.8(d)	6.99(d)	10.2(e)	
						J_{HP} = 12	J_{HP} = 8.2		
				9 H	9 H	6 H	1 H	2 H	
				$C(CH_3)_3$	$C(CH_3)_3$	—O—CH_3	arom.	—OH	
13b	24[b]	28.15	[d]	1.28(s)	1.4(s)	4.2(d of q)	6.99(d)	10.3(e)	
						J_{HP} = 13.5	J_{HP} = 8.0		
						J_{HH} = 4.5			
			6 H	9 H	9 H	4 H	1 H	2 H	
			CH_3	$C(CH_3)_3$	$C(CH_3)_3$	—O—CH_2	arom.	—OH	
13c	24[b]	24.22	1.24(d)	1.28(s)	1.51(s)	4.75(d of sept)	6.99(d)	8.8(e)	
			J_{HH} = 6.0			J_{HP} = 13.5	J_{HP} = 8.5		
						J_{HH} = 6.0			
			12 H	9 H	9 H	2 H	1 H	2 H	
			$CH(CH_3)_2$	$C(CH_3)_3$	$C(CH_3)_3$	$CH(CH_3)_2$	arom.	—OH	

[a] See experimental for details of NMR experiments.
[b] The solvent is $CDCl_3$.
[c] The solvent is CD_2Cl_2.
[d] The hydrogens of the CH_3 group are partially obscured by those of the tert-butyl groups.
[e] The resonance is very broad.

TABLE 3

^{13}C NMR Spectral Data[a]

Cpd./C[b]	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
7a[c]	31.9(d) J = 3.8	32.1	34.7(d) J = 6.9	35.1	56.1(d) J = 5.4		105.3(d) J = 15	114.3	132(d) J = 6.4	139(d) J = 3.0	143.9	144.1
b[c]	30.2(d) J = 3.7	31.9	34.7(d) J = 4.5	35.2	64.3(d) J = 10.9	16.9(d) J = 8.4	105.3(d) J = 15.2	114.3	132(d) J = 12.7	139.5(d) J = 4.9	143.4	145.8
c[d]	29.9(d) J = 3.2	31.8	34.6	35.3	65.5 (d of d) J = 24.8 J = 10.0	124.4 (d of q) J = 227.2 J = 10.0	105.9(d) J = 15	116.4	133.7(d) J = 10.7	138.9(d) J = 3.8	141.7 (d) J = 3.5	146.4 (d) J = 3.5
d[d]	29.3(d) J = 3.2	31.4	34.4	35.1	73.1 (d of spt.) J = 24.8 J = 11.0	127.5 (d of q) J = 277.3 J = 10.5	106.0(d) J = 15.0	117.4	133.6(d) J = 10.7	138.8(d) J = 4.1	141.5 (d) J = 5.0	146.2 (d) J = 4
13a	28.9	29.5(d) J = 7.3	32.5	37.7(d) J = 3.0	52.7(d) J = 3.5	106.1	117.4	138.3(d) J = 2.9	141.9(d) J = 15.0	143(d) J = 7.3	151(d) J = 8.1	

[a] See experimental for details of NMR experiments. Since all spectra are proton decoupled, the coupling constants listed reflect coupling to fluorine and phosphorus.

[b] The numbering system is as in Figures 1, 2.

[c] The solvent is $CDCl_3$.

[d] The solvent is CD_2Cl_2.

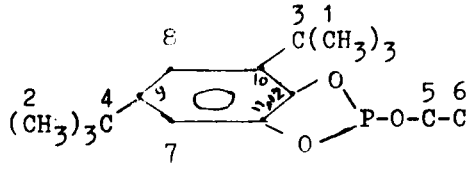


FIGURE 1

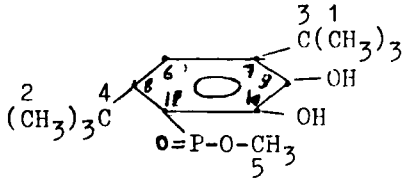
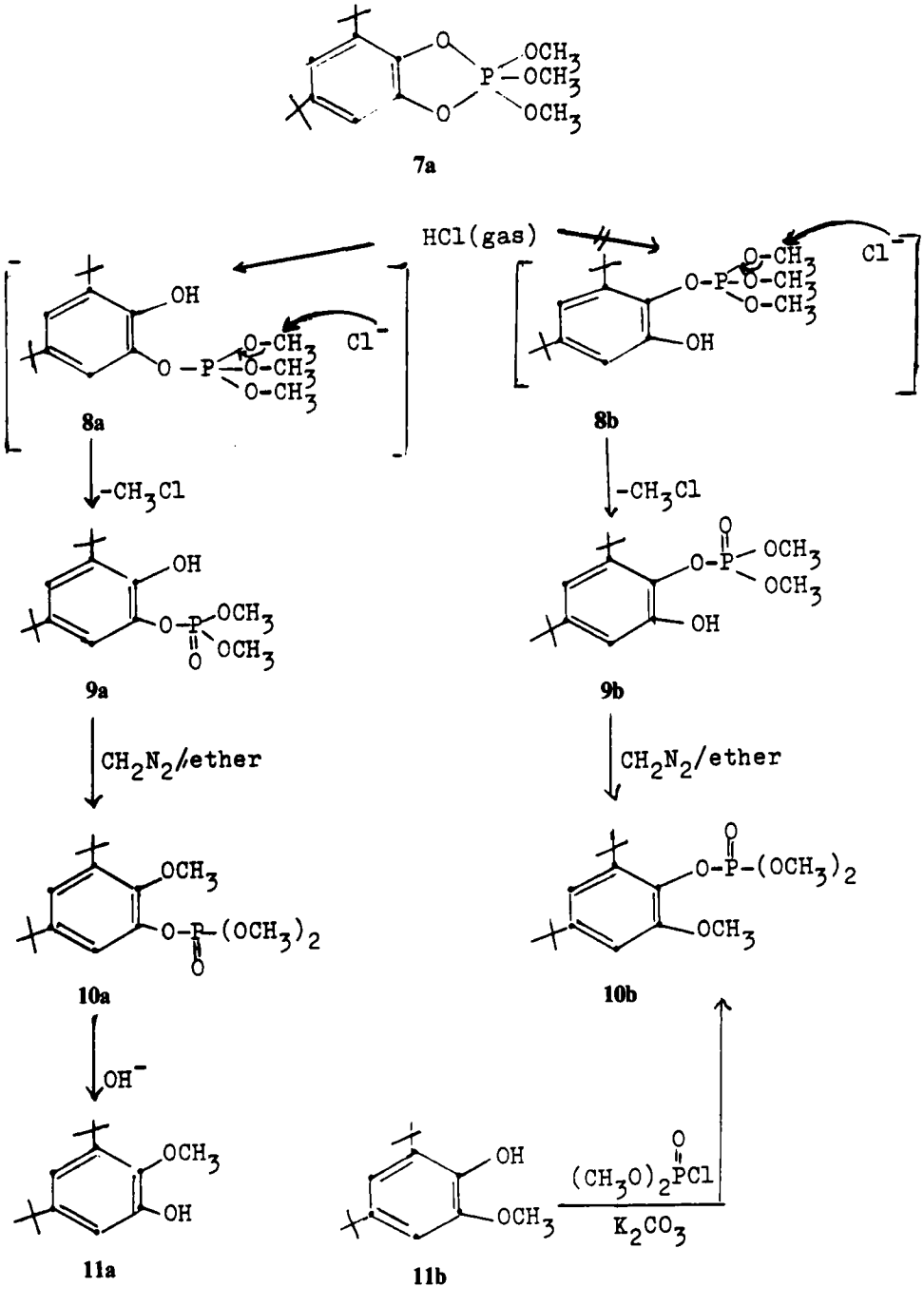


FIGURE 2

ppm; denoting that the three trifluoroethoxy groups are equivalent. At −93°C, however, these triplets degenerated to a broad featureless absorption; denoting thus that intramolecular ligand reorganization (pseudorotation) in **7c** has been slowed down upon lowering the temperature. However, such degeneration of the triplets may be attributed to a viscosity effect[3] since phosphorane **7c** crystallizes out at this temperature. In favor of this conclusion is the finding that variable temperature ^{19}F NMR spectral studies on a structurally-analogous pentaoxyphosphorane adduct of type **4** showed no evidence for ligand reorganization (pseudorotation) even at very low temperature.[5]

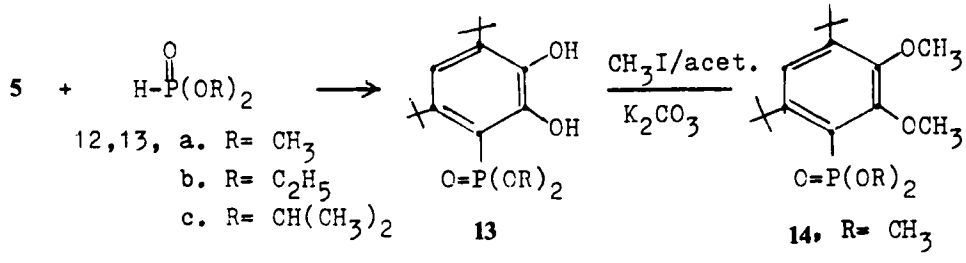
Moreover, the ^1H NMR spectrum of adduct **7c** (in CD_2Cl_2) at r.t. showed a single doublet of quartets at δ 4.45 (J_{HF} = 9.0 & J_{HP} = 4.2) assigned to three pairs of equivalent trifluoroethyl-CH_2 protons.

When adduct **7a** was treated with dry HCl gas in ether, it gave a colorless crystalline product "A" for which the *o*-quinol monophosphate structure **9** was assigned for the following reasons: (a) Compound **9** dissolves freely in dilute aq. alkali and exhibits a green color reaction with alcoholic ferric chloride solution. (b) Elemental analyses and molecular weight determination (MS) for **9**, corresponds to $C_{16}H_{27}O_5P$. (c) The ^{31}P NMR shift recorded for compound **9** was δ −4.02 ppm. This latter value is compatible with the phosphate shifts.[6] (d) The ^1H NMR



SCHEME 1

spectrum of **9** revealed the presence of signals at δ 3.8 [6 H, P(O)$(OCH_3)_2$, d; J_{HP} = 11.5 Hz] and δ 9.2 (OH, s, exchangeable with D_2O). The aromatic protons gave two doublets (each with J_{HH} = 4.0 Hz) at δ 6.23 (C-6) and δ 6.99 (C-4), respectively, while protons of the tert-butyl groups appeared as two singlets at δ 1.3 (9 H) and 1.6 (9 H). (e) The IR spectrum of **9** revealed presence of bands at 3500 cm^{-1} (OH), 1220 cm^{-1} (P=0, bonded[9]) and at 1035 cm^{-1} (P—O—CH_3). Structure **9a**, however, seems to represent the reaction product "A" of **7a** with HCl gas, more adequately than the other possible alternative form **9b** for the following reasons: (a) Upon methylation of product "A", it yielded a monomethyl ether "B" which has been found isomeric ($C_{17}H_{29}O_5P$) but not identical with the one obtained *via* phosphorylation of 2-methoxy-4,6-di-tert-butylphenol (**11b**)[10] with dimethylphosphorochloridate in acetone in the presence of K_2CO_3 (Scheme 1). (b) Upon alkali hydrolysis, the monomethyl ether "B" afforded a new phenolic substance isomeric (but not identical) with **11b** and proved to be 2-methoxy-3,5-di-tert-butylphenol (**11a**) (experimental). Based upon these arguments, there is no plausible alternative other than that the oxyphosphorane ring in **7a** is cleaved by HCl gas to give an *o*-quinol monophosphate of type **9a** (and not **9b**) which upon methylation, yields a monomethyl ether of type **10a** (and not **10b**). Consequently, the transformation step **7a** → **9a** should involve, presumably, a nucleophilic attack of the chloride ion on the activated alkyl group of a trialkoxyaryloxyphosphonium salt[11] (cf. **8a**). This type of transformation, which represents a convenient route to *o*-quinol monophosphates of interest in biological chemistry,[12] has prompted us to attempt preparing compounds of type **9** *via* an independent procedure which comprises reacting quinone **5** directly with dialkyl phosphites (**12a–c**). We have found that the reaction of quinone **5** with dimethyl phosphite (**12a**) proceeds smoothly in CH_2Cl_2 at r.t. However, the predicted *o*-quinol monophosphate **9a** (or **9b**) was not obtained. Instead, a colorless crystalline compound isomeric ($C_{16}H_{27}O_5P$) but not identical with **9**, was obtained almost as a sole product. This latter was assigned structure **13a** for the following reasons: (a) The ^{31}P NMR shift recorded for **13a** was δ +29.8 ppm which is consistent with the phosphonate structure.[6,13] (b) Its ^1H NMR spectrum exhibited a doublet (J_{HP} = 12 Hz) centred at δ 3.8 due to the two (OCH_3) groups attached to phosphorus. Moreover, the doublet at δ 6.23 assignable to proton on C-6 in the ^1H NMR spectrum of quinone **5**,[14] was absent in the spectrum of adduct **13a**. The proton on C-4 in **13a** also appeared as a doublet (J_{HP} = 8.0 Hz) due to coupling with phosphorus[15,16] at δ 6.99, while protons of the tert-butyl groups appeared as two singlets at δ 1.2 (9 H) and 1.34 (9 H). Moreover, the broad signal present at δ 10.2 (exchangeable with D_2O) accounted for two phenolic OH groups. (c) The IR

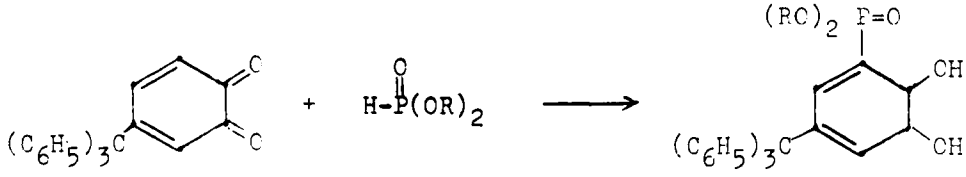


spectrum of **13a**, showed strong bands at 3550 cm^{-1} (OH), 1220 cm^{-1} (P=O, bonded) and at 1035 cm^{-1} (P—O—CH_3). (d) Adduct **13a** reacted with methyl iodide in presence of acetone and anhydrous K_2CO_3, to give the corresponding dimethyl ether **14** which had analytical and spectroscopic data in complete accordance with the proposed structure (experimental).

Even though free radical (FR) mechanisms are frequently observed in the reaction of dialkyl phosphites with quinones,[17] it seems that this mechanism is not involved in the reaction of quinone **5** with the same reagents since it proceeds to yield **13** both in the dark and in presence of free radical inhibitors such as hydroquinone.

CONCLUSION

From the foregoing observations, it is evident that variable temperature NMR studies on pentaoxyphosphoranes **7** did not show inhibition of pseudorotation even at very low temperatures (−93°C). This shows that steric effect of the substituents on the benzene ring is not the only factor to cause such inhibition. It seems that incorporation of a rigid ring in the pentaoxyphosphorane structure (cf. 1)[4] is an important requisite to slow pseudorotation in these systems. Although quinone **5** reacts with trialkyl phosphites to give pentaoxyphosphorane 1:1 adducts, as frequently observed with *o*-quinones,[11,18-20] an anomalous behaviour, however, was shown toward dialkyl phosphites, where ring-attack occurs to give phosphonate 1:1 adducts of type **13**. It is worthy of mention here that ring attack by dialkyl phosphites on asymmetrically substituted *o*-quinones has been also observed in the case of 4-triphenylmethyl-1,2-benzoquinone (**15**) where dialkyl phosphonate 1:1 adducts of type **16** were produced.[21]



15 **12**, R= alkyl **16**, R= alkyl

EXPERIMENTAL

The appropriate precautions in handling moisture-sensitive compounds were observed. Solvents were dried by standard techniques including high vacuum procedures. All melting points are uncorrected.

Hydrogen-1 NMR spectra were obtained on Varian T-60 and FT-80 spectrometers. Chemical shift values were recorded in δ ppm relative to internal tetramethylsilane. ^{31}P, ^{19}F and ^{13}C spectra were recorded with a Varian FT-80 spectrometer equipped with a variable-temperature broadband probe. ^{31}P NMR spectra are recorded relative to external H_3PO_4 (85%). ^{19}F chemical shifts are recorded relative to external trifluoromethane. ^{13}C NMR spectra are recorded relative to internal TMS. The mass spectra were run at 70 eV on Kratos equipment provided with a data system.

Reagents. The trialkyl phosphites were purified by treatment with sodium ribbon followed by fractional distillation. The dialkyl phosphites and dimethyl phosphorochloridate were freshly prepared.

Action of Trialkyl Phosphites on 3,5-Di-tert-Butyl-o-Benzoquinone (**5**).

General Procedure. To a stirred solution of (0.02 mol) of the quinone **5*** in 10 ml of CH_2Cl_2 at $-50°C$ was added a solution of (0.021 mol) of the trialkyl phosphite (trimethyl,[22] triethyl,[22] 2,2,2-trifluoroethyl[23] and 1,1,1,3,3,3-hexafluoroisopropyl[24] phosphite, respectively) in CH_2Cl_2 (3 ml). The reaction mixture was allowed to warm to r.t (3 hr), then it was further stirred for 1 hr. The removal of the solvent at 20°C, first at 20 mm and then at 0.05 mm left a yellow oil which became nearly colorless crystalline mass on adding a few mls of pentane. On crystallization from a suitable solvent it gave the colorless crystalline pentaoxyphosphoranes **7a–d** in colorless crystalline form. Percentage yields, physical and analytical data for compounds **7** are given in Tables 1, 2, 3.

Action of Dry Hydrogen Chloride on **7a**. A solution of compound **7a** (1.6 g) in ether (30 ml) was treated with an excess of hydrogen chloride gas at 10–15°C. The solution was evaporated at 20°C. Adding 5 ml of light petroleum afforded a crystalline residue which was recrystallized from cyclohexane to give 1-hydroxy-3,5-di-tert-butylbenzene-2-dimethyl phosphate (**9a**) (1.2 g; 75%), m.p. 67°C.

Anal. Calcd. for $C_{16}H_{27}O_5P$: C, 58.17; H, 8.23; P, 9.34. Found: C, 57.62; H, 8.17; P, 9.07. IR (KBr): Bands at 3500 (OH), 1220 (P=O) and 1035 cm^{-1}(P—O—CH_3). ^1H NMR ($CDCl_3$): Signals at 1.3 and 1.6 (18 H, tert-butyl, two (s)); 3.82 (6 H, (O)P(OCH_3)$_2$, d, J_{HP} = 11.5 Hz); 6.23 (1 H, proton on C-6, d of d, J_{HP} = 8 Hz, J_{HH} = 4.0); 6.99 (1 H, proton on C-4, d, J_{HH} = 4.0 Hz); 9.2 (OH, bs, exchangeable with D_2O). ^{31}P ($CDCl_3$): δ −4.02 ppm.

Action of Diazomethane on **9a**. A solution of **9a** (0.8 g) in ether (15 ml) was treated with an ethereal diazomethane solution (from 5 g *N*-nitrosomethylurea), then kept at 5°C for 6 hr. After removal of ether, the residue was crystallized from light petroleum to give **10a** (90%) as colorless crystals m.p. 55°C. Anal. Calcd. for $C_{17}H_{29}O_5P$: C, 59.28; H, 8.49; P, 8.99. Found: C, 59.01; H, 8.38; P, 8.65. MS: m/e 344 (M^+, 45%). IR (KBr): Bands at 1280 (P=O) and 1025 cm^{-1} (P—OCH_3). ^1H NMR ($CDCl_3$): Signals at 1.3 and 1.65 (18 H, tert-butyl, 2(s)); 3.8 (3 H, OMe, s); 3.88 (6 H, (O)P(OCH_3), d, J_{HP} = 12 Hz); 6.23 (1 H, proton on C-6, d of d, J_{HP} = 8.0, J_{HH} = 4.0); 6.99 (1 H, proton on C-4, d, J_{HH} = 4.0 Hz). ^{31}P NMR ($CDCl_3$): δ −4.65 ppm.

Action of Alkali on **10a**. A mixture of **10a** (0.8 g) and 10% NaOH aq. (30 ml) was refluxed for 2 hr. After cooling the solution was acidified with 15% HCl. The residue (ca. 0.5 g, 85%) was distilled at 152–155°C/13 mm to give **11a** as pale yellow liquid. Calcd. for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 75.94; H, 10.02. MS: m/e 236 (M^+, 40%). IR(KBr): OH band at 3530 cm^{-1}.

Action of Dimethylphosphorochloridate on 2-Methoxy-4,6-Di-tert-Butylphenol (**11b**). To a stirred solution of **11b** (2.4 g; 0.01 mol) in dry acetone (100 ml) was added 5 g of dry K_2CO_3. Stirring was continued at r.t. for 1 hr. Dimethylphosphorochloridate[25] (2 g, 0.012 mol) was added and the mixture refluxed for 10 hr. After removal of the inorganic material by filteration, the volatile materials were removed from the filtrate under reduced pressure. The residual material was collected (2.6 g, 80%) and recrystallized from pentane to give **10b** as colorless crystals, m.p. 62°C. Anal. Calcd. for: $C_{17}H_{29}O_5P$, C, 59.28; H, 8.49; P, 8.99. Found: C, 59.57; H, 8.41; P, 8.76. MS: m/e 344 (M^+, 25%).

IR (KBr): Bands at 1300 (P=O) and 1050 cm^{-1} (—P—O—CH_3). ^1H NMR($CDCl_3$): Signals at 1.3 and 1.6 (18 H, tert-butyl, 2(s)); 3.78 (3 H, OMe, s); 3.87 (6 H, (O)P(OCH_3)$_2$, d, J_{HP} = 11.5 Hz); 6.23 and 6.99 (2 H, aromatics, 2(d) each with J_{HH} = 4 Hz).

Action of Dialkyl Phosphites on **5**. To a stirred solution of quinone **5** (0.02 mol) in CH_2Cl_2 at r.t. was added a solution of (0.022 mol) of the dialkyl phosphite (dimethyl-, diethyl- and diisopropyl phosphite,[26] respectively) in CH_2Cl_2 (3 ml). The reaction mixture was kept overnight (until the red solution became colorless). After removing the volatile materials, *in vacuo*, the oily residue was triturated with light petroleum and left to cool in the ice-chest. The solid so formed, was collected, dried, and recrystallized from a suitable solvent to give compounds **13**. Percentage yields, physical and analytical data for the colorless adducts **13a–c** are given in Tables I, II, III. Compounds **13** respond positively to the $FeCl_3$ reaction, giving a purple color.

Parallel experiments in the dark and/or in the presence of hydroquinone, resulted in the isolation and identification (comparative m.p. and infra-red spectra) of compounds **13** in comparable yields.

Methylation of Phosphonate **13a**. To a stirred solution of **13a** (1.1g, 0.005 mol) in dry acetone (100 ml) was added 5 g of K_2CO_3. Stirring was continued at r.t. for 1 hr. Freshly distilled CH_3I (2.1 g, 0.015 mol)

*Commercially available from Aldrich Company.

was added dropwise and the mixture gently heated under reflux for 12 hr. The inorganic and volatile materials were removed to give **14** (0.8 g, 70%) in a semi-solid form which solidified after trituration with cold pentane. This material was crystallized from pentane to yield **14** as white crystals m.p. 72°C. Anal. Calcd. for $C_{18}H_{31}O_5P$: C, 60.32, H, 8.72; P, 8.64. Found: C, 60.00; H, 8.68; P, 8.47. MS: m/e 358 (M^+, 38%).

IR(KBr): Bands at 1300 (P=O) and 1035 cm^{-1} (P—O—CH_3). ^1H NMR($CDCl_3$): Signals at 1.37 and 1.55 (18 H, tert-butyl, 2(s); 3.77 (6 H, $(O)P(OCH)_3)_2$, d, J_{HP} = 12 Hz); 3.78 and 3.79 (6 H, OMe, 2(s)); 7.1 (1 H, proton on C-4, d, J_{HH} = 8.0 Hz). ^{31}P NMR ($CDCl_3$): +19.84 ppm.

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