

90, and 140 hr., respectively, at reflux temperature (in the case of F) and at 45° (in the case of M and N). The residues isolated after complete evaporation of ethyl iodide from the reaction mixture were by infrared analysis found to be the unreacted starting product, recovered in amounts of 91–94% by weight.

**Bromoallylmercaptotriaminophosphoranes**,  $[(>N)_3PSC_3H_5]^+Br^-$ .—Mixtures containing allyl bromide (1.5 g.-moles) and the nucleophiles A, B, D, and G (0.15 g.-mole each) were refluxed with agitation for 125, 170, 170, and 60 hr., respectively. The reaction mixtures were worked up like those obtained with ethyl iodide (*vide supra*). Obtained were:  $[(H_2N)_3PSC_3H_5]^+Br^-$  (III, 33.7 g., 97%, m.p. 171–172°),  $[(CH_3NH)_3PSC_3H_5]^+Br^-$  (VII, 40.7 g., 99%, m.p. 86–88°),  $[(C_6H_{11}NH)_3PSC_3H_5]^+Br^-$  (XII, 69 g., 96%, m.p. 112–114°), and  $\{[(CH_3)_2N]_2(C_2H_5NH)PSC_3H_5\}^+Br^-$  (XXII, 38 g., oil, 81%), respectively.

*Anal.* Calcd. for  $C_3H_{11}BrN_3PS$  (III): Br, 34.43; N, 18.10; S, 13.82. Found: Br, 34.8; N, 18.35; S, 13.95. Calcd. for  $C_6H_{17}BrN_3PS$  (VII): Br, 29.15; N, 15.33; S, 11.70. Found: Br, 30.0; N, 14.57; S, 10.99. Calcd. for  $C_{21}H_{43}BrN_3PS$  (XII): Br, 16.70; N, 8.78; S, 6.70. Found: Br, 16.9; N, 8.91; S, 7.04. Calcd. for  $C_9H_{23}BrN_3PS$  (XXII): Br, 25.43; N, 13.37; S, 10.20. Found: Br, 25.85; N, 13.76; S, 10.47.

Mixtures composed of allyl bromide (1.0 g.-mole) and the compounds H and N (0.15 g.-mole each) were heated to reflux with agitation for 50 and 200 hr., respectively. After complete evaporation of unreacted allyl bromide from the reaction mixtures the evaporation residues were by infrared analysis identified as unreacted starting products.

**Bromo-*n*-propylmercaptotriaminophosphoranes**,  $[(>N)_3PSC_3H_7-n]^+Br^-$ .—Mixtures consisting of *n*-propyl bromide (1.5 g.-moles) and the nucleophiles A, B, D, E, and G (0.15 g.-mole each) were refluxed for 100, 200, 170, 115, and 100 hr., respectively, with agitation and the resulting reaction mixture was worked up like those formed with ethyl iodide (*vide supra*). Obtained were:  $[(H_2N)_3PSC_3H_7-n]^+Br^-$  (IV, 32.7 g., 93%, m.p. 163–164°),  $[(CH_3NH)_3PSC_3H_7-n]^+Br^-$  (VIII, 38.8 g., 94%, m.p. 74–76°),  $[(C_6H_{11}NH)_3PSC_3H_7-n]^+Br^-$  (XIII, 70.5 g., 98%, m.p. 128–130°),  $[(C_6H_5-CH_2NH)_3PSC_3H_7-n]^+Br^-$  (XV, 73.5 g., 97%, m.p. 112–113°), and  $\{[(CH_3)_2N]_2(C_2H_5NH)PSC_3H_7-n\}^+Br^-$  (XXIII, 46.5 g., oil, 98%), respectively.

*Anal.* Calcd. for  $C_3H_{13}BrN_3PS$  (IV): Br, 34.14; N, 17.95; S, 13.70. Found: Br, 34.5; N, 17.78; S, 13.84. Calcd. for  $C_6H_{19}BrN_3PS$  (VIII): Br, 28.94; N, 15.22; S, 11.61. Found: Br, 29.1; N, 15.26; S, 12.1. Calcd. for  $C_{21}H_{43}BrN_3PS$  (XIII): Br, 16.63; N, 8.75; S, 6.67. Found: Br, 16.6; N, 8.52; S, 7.05. Calcd. for  $C_{24}H_{51}BrN_3PS$  (XV): Br, 15.84; N, 8.33; S, 6.36. Found: Br, 16.1; N, 8.35; S, 6.74. Calcd. for  $C_9H_{25}BrN_3PS$  (XXIII): Br, 25.27; N, 13.29; S, 10.14. Found: Br, 26.40; N, 13.52; S, 10.84.

Mixtures of *n*-propyl bromide (1.0 g.-mole) and the compounds F and H (0.1 g.-mole each) were heated at reflux temperature with agitation for 170 and 130 hr., respectively. The solids isolated from the reaction mixtures after complete removal of unreacted propyl bromide were found to consist of unreacted starting products, according to infrared analysis.

**Bromoisopropylmercaptotriaminophosphoranes**,  $[(>N)_3PSC_3H_7-i]^+Br^-$ .—Mixtures containing isopropyl bromide (1.0 g.-mole)

and the nucleophiles B, D, and E (0.1 g.-mole each) were heated with agitation to reflux for 160, 160, and 115 hr., respectively. The reaction mixtures produced were worked up as described with ethyl iodide (*vide supra*). Obtained were:  $[(CH_3NH)_3PSC_3H_7-i]^+Br^-$  (XXIV, 23 g., 83%, m.p. 98–100°),  $[(C_6H_{11}NH)_3PSC_3H_7-i]^+Br^-$  (XXV, 41.7 g., 87%, m.p. 120–122°), and  $[(C_6H_5-CH_2NH)_3PSC_3H_7-i]^+Br^-$  (XXVI, 38 g., 75%, m.p. 122–124°), respectively.

*Anal.* Calcd. for  $C_6H_{19}BrN_3PS$  (XXIV): Br, 28.94; N, 15.22; S, 11.61. Found: Br, 28.7; N, 14.98; S, 11.98. Calcd. for  $C_{21}H_{43}BrN_3PS$  (XXV): Br, 16.63; N, 8.75; S, 6.67. Found: Br, 16.4; N, 9.34; S, 7.12. Calcd. for  $C_{24}H_{51}BrN_3PS$  (XXVI): Br, 15.84; N, 8.33; S, 6.36. Found: Br, 15.9; N, 8.16; S, 6.71.

Mixtures of isopropyl bromide (1.0 g.-mole) and the compounds A, F, H, and N (0.1 g.-mole each) were heated at reflux temperature with agitation for 150 hr. The solid residues isolated by unreacted isopropyl bromide gave infrared spectra that were identical with the spectra of the phosphorothionates used as starting products.

**Chlorobenzylmercaptotriaminophosphoranes**,  $[(>N)_3PSC_2C_6H_5]^+Cl^-$ .—Mixtures composed of benzyl chloride (0.5 g.-mole) and the nucleophiles A and B (0.1 g.-mole each) were heated with agitation for 130 hr. at 95° and, respectively, for 170 hr. at 75°. After this treatment the mixtures were diluted with ligroin (0.5 l., b.p. 60–70°) and filtered. The solids thus isolated were dissolved in dimethylformamide (100 ml.) and the resulting solution diluted with ether (1 l.) to precipitate the onium derivatives. Obtained were:  $[(H_2N)_3PSC_2C_6H_5]^+Cl^-$  (V, 16.6 g., 70%, m.p. 144–146°) and  $[(CH_3NH)_3PSC_2C_6H_5]^+Cl^-$  (IX, 24.3 g., 87%, m.p. 156–158°).

*Anal.* Calcd. for  $C_7H_{13}ClN_3PS$  (V): Cl, 14.92; N, 17.68; S, 13.49. Found: Cl, 14.7; N, 17.67; S, 13.67. Calcd. for  $C_{10}H_{17}ClN_3PS$  (IX): Cl, 12.67; N, 15.02; S, 11.46. Found: Cl, 12.8; N, 14.67; S, 11.57.

A solution of compound N (0.1 g.-mole) in benzyl chloride (0.5 g.-mole) was heated with agitation at 75° for 170 hr. and then treated with ligroin as described with the compounds A and B. This caused formation of a precipitate which was identified as unreacted N (recovered in 20% yield).

**Reaction with *t*-Butyl Bromide**.—This bromide (1.3 g.-moles) was heated to reflux at atmospheric pressure with agitation in the presence of the compounds E, F, H, N, and  $[(CH_3)_2N]_3PO$  (0.1 g.-mole each). It was noticed that the reaction caused a rather steady evolution of a gas which was collected in a Dry Ice trap connected with the reflux condenser. This gas was by infrared analysis found to be isobutylene and was recovered in quantities of 0.54–0.6 g.-mole, after a total reaction time of 200 hr. The reaction mixture formed by this reaction was diluted with the threefold volume of ligroin (b.p. 60–70°) and filtered. The salts thus isolated from the five experiments were identified as the hydrobromides of benzylamine, *p*-chloroaniline, diethylamine, piperidine, and dimethylamine, respectively. They were recovered in quantities of 0.25–0.3 g.-mole. The filtrate was fractionated under reduced pressure and gave  $PSBr_3$  (b.p. 84° at 10 mm.) in quantities of 18–24 g. The run involving the compound  $[(CH_3)_2N]_3PO$  gave 20 g. of phosphoryl bromide.

The melting points given were not corrected.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE STATE UNIVERSITY OF NEW YORK AT STONY BROOK, N. Y., AND THE ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO, ILL.]

## Organic Compounds with Pentavalent Phosphorus. VIII.<sup>1</sup> Cyclic Unsaturated Oxyphosphoranes from the Reaction of Tertiary Phosphite Esters with *o*-Quinones and with $\alpha$ -Diketones

BY FAUSTO RAMIREZ<sup>2</sup> AND N. B. DESAI

RECEIVED MAY 2, 1963

Tertiary phosphite esters,  $(RO)_3P$ , react with *o*-quinones and with  $\alpha$ -diketones, yielding 1:1 adducts. Six crystalline and three liquid adducts are described. The reactions are exothermic and the products are obtained in nearly quantitative yield. The adducts are stable, if protected against moisture and oxygen. The infrared, Raman,  $P^{31}$  n.m.r., and  $H^1$  n.m.r. spectra suggest that the 1:1 adducts have a cyclic unsaturated oxyphosphorane structure, in which five oxygen atoms are covalently bound to phosphorus.

A phosphorus–oxygen bond is formed in the reaction of triphenylphosphine with the substituted *p*-quinone

chloranil; however, a phosphorus–carbon bond is established in the reaction of this phosphine with *p*-benzo-

(1) (a) Part VII: F. Ramirez, N. B. Desai, and N. Ramanathan, *Tetrahedron Letters*, No. 5, 323 (1963); (b) part VI: F. Ramirez, N. Ramanathan, and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 1317 (1962); (c) part V: F. Ramirez and N. Ramanathan, *J. Org. Chem.*, **26**, 3041 (1961); (d) part IV: F. Ramirez, N. B. Desai, and R. B. Mitra, *J. Am. Chem. Soc.*, **83**, 492 (1961); (e) part III: F. Ramirez, R. B. Mitra, and N. B. Desai, *ibid.*, **82**, 5763 (1960); (f)

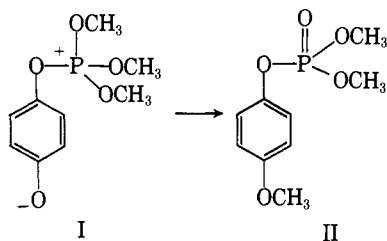
(2) Alfred P. Sloan Fellow 1961–1963. Acknowledgment is made to the Donors of the Petroleum Research Fund Administered by the American Chemical Society (Grant 286-A), to the Cancer Institute of the National Institutes of Health (Grant CY-4769), and to the National Science Foundation (Grant G9917) for generous support of this research.

TABLE I  
 1:1 ADDUCTS FROM THE REACTION OF TERTIARY PHOSPHITE ESTERS WITH *o*-QUINONES AND WITH  $\alpha$ -DIKETONES

1:1 adduct	Carbonyl compound	R in (RO) <sub>3</sub> P	M.p. or b.p. (mm.), <i>n</i> <sub>D</sub> <sup>25</sup>	Mol. formula	Calcd.			Found			P <sup>21</sup> n.m.r. <sup>a</sup>	Infrared bands, <sup>b</sup> $\mu$
					C	H	P	C	H	P		
VII <sup>c</sup>	Phenanthrenequinone	CH <sub>3</sub>	74–75 <sup>d</sup>	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub> P <sup>e</sup>	61.5	5.2	9.3	61.8	5.4	9.5	+49	3.45(w), 6.04(mw), 6.23(w), 6.62(w), 6.87(mw), 7.24(ms), 7.50(w), 8.47(mw), 9.01(mw), 9.22(vs), 9.43(vs), 9.71(m), 10.5(mw)
VIII <sup>c</sup>	Phenanthrenequinone	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	105–106 <sup>d</sup>	C <sub>23</sub> H <sub>20</sub> O <sub>2</sub> P	66.4	6.9	7.4	66.0	6.8	7.3		3.35(w), 6.02(w), 6.2(vw), 6.62(vw), 6.85(w), 7.22(ms), 7.40(w), 8.50(w), 9.00(m), 9.40(w), 9.75(vs), 10.08(m), 10.2(w)
IX <sup>f</sup>	Phenanthrenequinone	C <sub>6</sub> H <sub>5</sub>	147–148 <sup>g</sup>	C <sub>22</sub> H <sub>18</sub> O <sub>2</sub> P	74.1	4.5	6.0	74.4	4.7	6.0	+58	3.35(w), 6.00(w), 6.25(m), 6.70(m), 6.85(w), 7.23(m), 8.30(s), 8.60(w), 9.80(m), 10.45(ms), 10.75(m)
X <sup>c,h</sup>	Benzil	CH <sub>3</sub>	49–50 <sup>d</sup>	C <sub>17</sub> H <sub>12</sub> O <sub>2</sub> P <sup>i</sup>	61.1	5.6	9.3	60.9	5.8	9.0	+53	3.35(w), 6.02(vw), 6.21(vw), 6.70(vw), 6.90(w), 7.72(w), 7.82(w), 8.45(w), 8.70(w), 9.18(vs), 9.42(vs), 9.73(w), 10.5(w)
XI <sup>h</sup>	Benzil	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	52–53 <sup>d</sup>	C <sub>23</sub> H <sub>20</sub> O <sub>2</sub> P	66.0	7.4	7.4	65.4	7.6	7.6	+54	3.35(w), 6.05(vw), 6.25(vw), 6.65(vw), 6.80(vw), 6.88(vw), 7.72(w), 7.82(w), 8.48(w), 8.70(m), 9.05(m), 9.75(vs), 10.20(m), 10.30(m)
XII <sup>f</sup>	Benzil	C <sub>6</sub> H <sub>5</sub>	99–100 <sup>d</sup>	C <sub>22</sub> H <sub>18</sub> O <sub>2</sub> P	73.8	4.8	6.0	73.5	4.9	6.0	+62	3.3(w), 6.0(vw), 6.22(m), 6.78(m), 8.23(s), 8.60(w), 8.82(w), 9.30(w), 9.70(w), 9.90(w), 10.40(s), 10.7(w)
XIII <sup>c,h</sup>	Biacetyl	CH <sub>3</sub>	45–47 (0.5) 1.4387 <sup>f</sup>	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub> P <sup>k</sup>	40.0	7.1	14.7	39.4	7.2	14.5	+53	3.38(w), 5.75(vw), 6.82(vw), 6.97(vw), 7.17(w), 7.72(w), 8.00(m), 8.43(w), 8.66(m), 9.18(vs), 9.30(vs), 10.0(m), 10.3(w)
XIV <sup>h</sup>	Biacetyl	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	82–83 (0.5) 1.4260	C <sub>13</sub> H <sub>20</sub> O <sub>2</sub> P	53.0	9.2	10.5	53.1	9.1	10.4	+51	3.32(w), 5.73(vw), 7.23(w), 7.75(w), 8.00(w), 8.48(w), 8.68(mw), 9.00(mw), 9.70(vs), 10.05(s), 10.30(m)
XV <sup>h</sup>	2,3-Pentanedione	CH <sub>3</sub>	59–62 (0.5) 1.4391	C <sub>8</sub> H <sub>12</sub> O <sub>2</sub> P	42.7	7.6	13.8	42.9	7.9	13.7	+46	3.38(w), 5.73(vw), 6.80(w), 6.92(vw), 7.72(w), 8.05(w), 8.43(w), 8.68(m), 9.15(vs), 9.30(vs), 9.5(m), 10.10(w), 10.15(w)

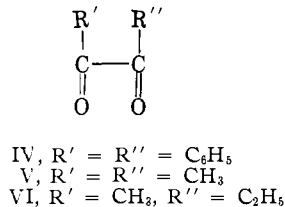
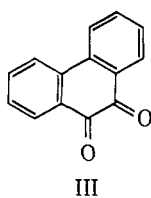
<sup>a</sup> Chemical shifts in p.p.m.  $\pm$  2, to high field of the external reference, 85% H<sub>3</sub>PO<sub>4</sub> at 16.2 Mc./sec.; the solids were examined in benzene, the liquids, neat. <sup>b</sup> Solutions in dry CCl<sub>4</sub>; 0.2-mm. cell, Perkin-Elmer Model 21 spectrometer (NaCl); the intensity of the bands (w = weak, m = medium, s = strong, v = very) is referred to the intensity of the main CH stretching band taken as "weak." <sup>c</sup> Prepared in benzene solution by procedure A (see Experimental). <sup>d</sup> Recrystd. from hexane. <sup>e</sup> Calcd. mol. wt. 332, found 303; all molecular weights by isothermal distillation in benzene. <sup>f</sup> Prepared at 110° in the absence of solvent. <sup>g</sup> Recrystd. from benzene-hexane. <sup>h</sup> Prepared at 20° or below, in the absence of solvent by procedure B (see Experimental). <sup>i</sup> Calcd. mol. wt. 334, found 293. <sup>j</sup> *d*<sub>D</sub><sup>25</sup> 1.166 g./cc. <sup>k</sup> Calcd. mol. wt. 210, found 210.

quinone.<sup>3</sup> The trialkyl phosphites have a greater tendency than the tertiary phosphines to form phosphorus-oxygen bonds with *p*-quinones. Trimethyl and triethyl phosphites react with chloranil,<sup>4</sup> with *p*-benzoquinone,<sup>5</sup> and with other *p*-quinones<sup>5</sup> to give alkyl ethers of *p*-quinolmonophosphates, for example II. There is evidence that the primary products of



these reactions are dipolar ions, for instance I, which undergo a subsequent alkyl-group translocation to give the stable ether-phosphates II.

Following these studies, we investigated the reactions of *o*-quinones and of  $\alpha$ -diketones with trialkyl phosphites



and with triary<sup>1</sup> phosphites. This paper describes the reactions of 9,10-phenanthrenequinone (III), benzil (IV), biacetyl (V), and 2,3-pentanedione (VI) with trimethyl, triisopropyl, and triphenyl phosphites. The structure of the products formed in these reactions has been elucidated by physical methods.<sup>6</sup>

## Results

Phenanthrenequinone (III) reacted with trimethyl phosphite, (CH<sub>3</sub>O)<sub>3</sub>P, at 20° in anhydrous benzene and formed a nearly colorless, crystalline, 1:1 adduct in quantitative yield. The properties of the adduct are listed in Table I. The cyclic unsaturated oxyphosphorane structure shown in formula VII of Chart I is assigned to this adduct, for reasons which are given in the Discussion section. The main feature of the oxyphosphorane structure is the presence in it of pentavalent phosphorus.

The reaction of triisopropyl phosphite was entirely analogous and gave the crystalline adduct VIII. Triphenyl phosphite seemed to be less reactive than the trialkyl phosphites, but it also afforded a 1:1 adduct IX.

The aromatic  $\alpha$ -diketone benzil (IV) reacted vigorously with trimethyl phosphite and produced a similar 1:1 adduct (X) in quantitative yield. This low-melting solid could be distilled *in vacuo* without change.

The reaction of trimethyl phosphite with the aliphatic  $\alpha$ -diketone biacetyl (V) was even more vigorous and afforded a colorless liquid 1:1 adduct (XIII). Other compounds of a similar type were prepared in nearly quantitative yield and are listed in Table I.

The 1:1 adducts are quite stable when kept under dry nitrogen. They are extremely sensitive to mois-

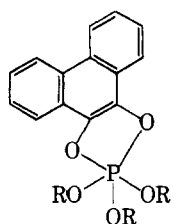
(3) (a) F. Ramirez and S. Dershowitz, *Chem. Ind. (London)*, 665 (1956); (b) *J. Am. Chem. Soc.*, **78**, 5614 (1956).

(4) (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 856 (1957); (b) *J. Am. Chem. Soc.*, **81**, 587 (1959).

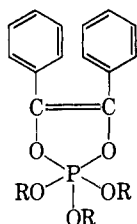
(5) F. Ramirez, E. H. Chen, and S. Dershowitz, *ibid.*, **81**, 4338 (1959).

(6) A preliminary account of parts of this work appeared in ref. 1g.

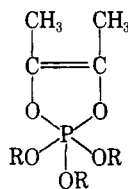
CHART I  
CYCLIC UNSATURATED OXYPHOSPHORANE STRUCTURES FOR THE  
*o*-QUINONE-TERTIARY PHOSPHITE AND THE  $\alpha$ -DIKETONE-TERTIARY  
PHOSPHITE 1:1 ADDUCTS



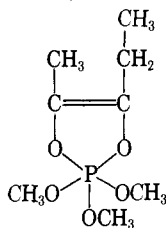
VII, R = CH<sub>3</sub>  
VIII, R = *i*-C<sub>3</sub>H<sub>7</sub>  
IX, R = C<sub>6</sub>H<sub>5</sub>



X, R = CH<sub>3</sub>  
XI, R = *i*-C<sub>3</sub>H<sub>7</sub>  
XII, R = C<sub>6</sub>H<sub>5</sub>



XIII, R = CH<sub>3</sub>  
XIV, R = *i*-C<sub>3</sub>H<sub>7</sub>

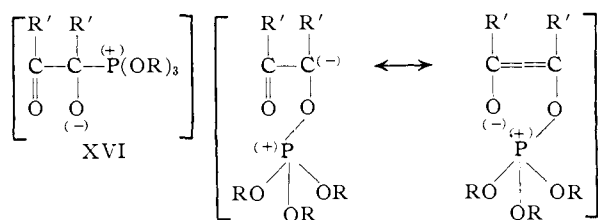


XV

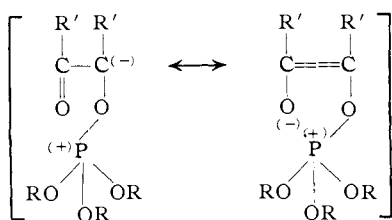
ture and react with dry oxygen and with a number of other reagents. The adducts are remarkably soluble in most organic solvents, including hexane, and can be recrystallized without change.

### Discussion

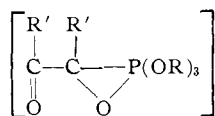
A satisfactory structure for the 1:1 adducts formed in the reaction of tertiary phosphite esters with *o*-quinones and with  $\alpha$ -diketones must answer three questions: (1) Is a new phosphorus-carbon bond or a new phosphorus-oxygen bond formed? (2) Is the phosphorus in the adducts tetravalent or pentavalent? (3) If the phosphorus is pentavalent, is it part of a trigonal bipyramid, of a square pyramid, or of another type of configuration? The latter point will not be discussed further in this paper. Questions 1 and 2 lead to a choice between structures XVI, XVII, XVIII, and XIX.



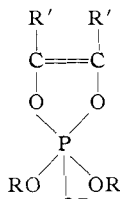
XVI



XVII



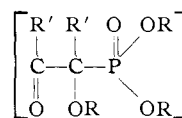
XVIII



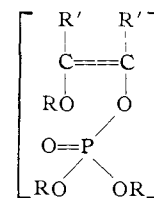
XIX

Furthermore, two additional isomeric phosphate ester structures, XX and XXI, should be considered, since an alkyl-group translocation is known<sup>4,5</sup> to occur in the reaction of trialkyl phosphites with *p*-quinones (I  $\rightarrow$  II)

We believe that the physical properties of the adducts point to the cyclic unsaturated oxyphosphorane structure XIX. In other words, the phosphorus atom of



XX



XXI

the trialkyl phosphite becomes covalently bound to five oxygen atoms in the adduct as a result of a reaction which occurs at room temperature and which is quite exothermic. Pentavalent phosphorus seldom has been observed among stable organic compounds; the only authentic case so far described is that of pentaphenylphosphorane,<sup>7</sup> with five phosphorus-carbon bonds.

**The 1:1 Biacetyl-Trimethyl Phosphite Adduct (XIII).**  
**Infrared Spectrum.**—The spectrum of this liquid adduct in carbon tetrachloride solution is reproduced in Fig. 1. At the concentration that must be employed in order to obtain the complete spectrum in the 3–10  $\mu$  region, there is practically no absorption in the carbonyl region, 5.6–6.0  $\mu$ . The very weak peak at 5.75  $\mu$  (1740  $\text{cm}^{-1}$ ) seems to be genuine and will be discussed below. However, the weak band which is sometimes observed at 5.81  $\mu$  (1720  $\text{cm}^{-1}$ ) is probably due to impurities formed as a result of hydrolysis or of other reactions.<sup>1b,f</sup>

The absence of a strong carbonyl band in the infrared excludes structures XVI, XVIII, and XX from further consideration. These structures have been proposed by Kukhtin<sup>8</sup> and his co-workers on several occasions.

The P=O stretching vibration in phosphate esters gives rise to a strong band in the region 7.42–8.00  $\mu$  (1350–1250  $\text{cm}^{-1}$ ).<sup>9a,f</sup> Although the biacetyl adduct XIII has bands in this region, their shape and intensity are not those of a typical phosphate ester. This point is discussed further in the next section.

The P–O–CH<sub>3</sub> group of trimethyl phosphate absorbs<sup>9a</sup> very strongly at 9.55  $\mu$  (1045  $\text{cm}^{-1}$ ). The strongest bands of the adduct XIII are at 9.18 (1090) and 9.30  $\mu$  (1075  $\text{cm}^{-1}$ ), significantly lower than the band of trimethyl phosphate. This relationship between a trialkyl phosphite adduct and the corresponding phosphate ester appears to be more general.

Structure XXI, which is a methyl phosphate ester, is inconsistent with the infrared spectrum of adduct XIII.<sup>10</sup> The phosphate structure XXI has been advocated by Kukhtin and co-workers<sup>8</sup> in some of their publications.

There is no close model for the type of carbonyl absorption which is to be expected from the open dipolar structure XVII. Perhaps a reasonable approximation is the carbonyl of the phosphineacetylmethylene XXII, which appears<sup>11</sup> as a strong band at 6.5  $\mu$ .

(7) (a) G. Wittig and M. Rieber, *Ann.*, **562**, 187 (1949); (b) P. J. Wheatley and G. Wittig, *Proc. Chem. Soc.*, 251 (62); (c) see review by J. R. Van Wazer, *J. Am. Chem. Soc.*, **78**, 5709 (1956).

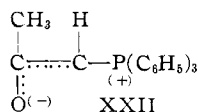
(8) (a) V. A. Kukhtin, K. M. Kirillova, and R. R. Shagidullin, *Zh. Obshch. Khim.*, **32**, 649 (1962); *Chem. Abstr.*, **58**, 546h (1963); (b) V. A. Kukhtin and J. Orekova, *Zh. Obshch. Khim.*, **30**, 1208 (1960); *J. Gen. Chem. U.S.S.R.*, **30**, 1229 (1960); *Chem. Abstr.*, **55**, 358i (1961); (c) V. A. Kukhtin, *Dokl. Akad. Nauk S.S.S.R.*, **121**, 466 (1958); *Chem. Abstr.*, **53**, 1105b (1959); (d) V. A. Kukhtin, K. M. Kirillova, R. R. Shagidullin, Yu. Yu. Samitov, N. A. Lyazima, and N. F. Rahova, *Zh. Obshch. Khim.*, **32**, 2039 (1962); *Chem. Abstr.*, **58**, 4543a (1963).

(9) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., 1958, Ch. 18; (b) p. 315; (c) p. 70; (d) p. 34; (e) p. 326; (f) R. C. Gore and E. S. Waight in "Determination of Organic Structures by Physical Methods," Vol. 1; E. A. Braude and F. C. Nachod, Ed., Academic Press, Inc., New York, N. Y., 1955, p. 208.

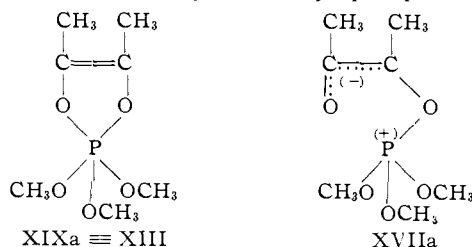
(10) Structures XX and XXI have been ruled out also on chemical grounds, since the group (RO)<sub>2</sub>P< was found to be intact in the adducts; cf. ref. 1d,e,f.

(11) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

Clearly, there is no absorption of this type in Fig. 1.



We conclude that the absence of strong carbonyl absorption in the entire region 5.6–6.6  $\mu$  of Fig. 1 favors the cyclic unsaturated oxyphosphorane structure (XIXa  $\equiv$  XIII) over the open dipolar structure (XVIIa) for the biacetyl-trimethyl phosphite adduct.



**Raman Spectrum.**—The oxyphosphorane structure for the biacetyl adduct XIII implies the presence of a C=C group in the molecule. The stretching vibrations of "normal" isolated olefinic double bonds appear in the region 5.95–6.17  $\mu$  (1680–1620  $\text{cm}^{-1}$ ).<sup>9d</sup> This band is weak, and its intensity is reduced by the symmetry around the bond. The frequency of the C=C stretching vibration increases to 1730–1780  $\text{cm}^{-1}$  when two or more fluorine atoms are substituted on the carbon atoms of the double bond.<sup>9d</sup> This shortening of the double bond is not well understood.

The biacetyl adduct XIII gave rise to a very weak band at 5.75  $\mu$  (1740  $\text{cm}^{-1}$ ) in the infrared. Therefore, we examined the Raman spectrum<sup>12</sup> of this compound in order to obtain more information on the origin of this band; the data are summarized in Table II.

TABLE II

RAMAN SPECTRUM OF THE 1:1 BIACETYL-TRIMETHYL PHOSPHITE ADDUCT (XIII)

Determined in a Cary Model 81 spectrometer on a 5-cc. sample of the liquid<sup>a</sup> (7-mm. sample cell); slit: 10  $\text{cm}^{-1}$  (double) in the 4000–1350  $\text{cm}^{-1}$  region, 5  $\text{cm}^{-1}$  (double) in the 1350–0  $\text{cm}^{-1}$  region; wave numbers (relative intensities).<sup>b</sup> When the line is polarized, *i.e.*, when the depolarization factor  $\rho < 0.8$ , the value of ( $\rho$ ) is also included.

2990 (175) (0.5); 2956 (313); 2927 (325); 2887 (144) (0.4); 2856 (156) (0.3); 1743 (162) (0.4); 1456 (183); 1393 (79); 1290 (4.0); 1240 (3.6); 1175 (4.0); 1155 (4.4); 1095 (5.6); 1065 (5.5); 1037 (6.0); 994 (4.2); 845 (1.7); 820 (2.0); 760 (3.0); 720 (10.0) (0.3); 575 (1.7); 594 (4.0); 581 (5.1); 540 (4.2) (0.35); 440 (4.0) (0.5); 365 (1.0) (0.4); 255 (2.6)

<sup>a</sup> There was little scattering and fluorescence; no zero suppression was used until narrow-slit, high-gain conditions. <sup>b</sup> The weakest line in the spectrum at 365  $\text{cm}^{-1}$  was given the arbitrary value of 1.0.

The eighteen bands present in the infrared spectrum of a  $\text{CCl}_4$  solution of XIII in the region 3–12.5  $\mu$  were also found in the Raman spectrum of the pure liquid; bands that were strong in the infrared appeared weak in the Raman and *vice versa*. Nine additional Raman lines could be seen above 12.5  $\mu$  (below 800  $\text{cm}^{-1}$ ).

The adduct gave rise to a relatively strong and polarized Raman line<sup>12</sup> at 1743  $\text{cm}^{-1}$ , which supports the presence of an olefinic C=C in the adduct XIII.

It should be noted that four of the low-frequency Raman lines are polarized, suggesting that they arise from totally symmetrical vibrations.<sup>12</sup> The liquid

(12) (a) F. F. Cleveland in ref. 9f, Ch. 6; (b) R. N. Jones and C. Sandorfy, in "Chemical Applications of Spectroscopy," W. West, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, Ch. 4, *cf.* p. 368; (c) A. B. F. Duncan, *ibid.*, Ch. 3, *cf.* pp. 206, 230.

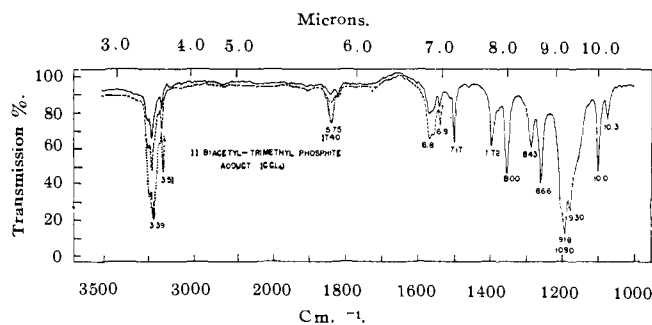


Figure 1.

showed no fluorescence in the determination of the Raman spectrum.

**$\text{P}^{31}$  Nuclear Magnetic Resonance.**<sup>13b, 14, 15</sup>—The signal due to the  $\text{P}^{31}$  n.m.r. is at a considerably higher field in the biacetyl adduct XIII than in 85% phosphoric acid, which is used as external reference. The positive chemical shift of this and of other adducts is given in Table I.<sup>15a</sup>

The  $\text{P}^{31}$  nucleus is more shielded in the adducts than in phosphoric acid. It is not possible, at present, to relate chemical shifts to molecular structure in all valence states of phosphorus<sup>15</sup>; therefore, to derive structural information from the  $\text{P}^{31}$  n.m.r. data in Table I, some comparisons with related compounds will be made. (All values of the chemical shift,  $\delta$ , are relative to phosphoric acid.) The largest positive chemical shift among compounds having four oxygens bonded to phosphorus has been observed<sup>13b, 14, 15</sup> in triphenyl phosphate,  $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$ ,  $\delta = +17$  p.p.m. Triphenyl phosphite gives a large negative shift,  $(\text{C}_6\text{H}_5\text{O})_3\text{P}$ ,  $\delta = -126$  p.p.m. A similar situation is observed in the series of alkyl esters:  $(\text{C}_2\text{H}_5\text{O})_3\text{PO}$ ,  $\delta = +1$  p.p.m.;  $(\text{C}_2\text{H}_5\text{O})_3\text{P}$ ,  $\delta = -137$  p.p.m. Thus, the effect on the  $\text{P}^{31}$  magnetic shielding caused by the introduction of a fourth oxygen atom on a tertiary phosphite ester is to produce a positive chemical shift ( $\Delta\text{PO-P} = +143$  and  $+138$  p.p.m. in the above examples).

We should like to know the effect on the  $\text{P}^{31}$  magnetic shielding caused by the introduction of a fourth alkoxy group on a trialkyl phosphite; however, data for tetraalkoxyphosphonium salts  $[(\text{RO})_3\text{POR}]^+\text{X}^-$  are not available and, for reasons inherent to this type of structure, not easily obtainable. It would be surprising, however, if the tetraalkoxyphosphonium salts were to give positive chemical shifts, relative to phosphoric acid (or to the phosphate esters), since in these phosphonium salts there is little opportunity for the fourth oxygen to contribute to the shielding of the phosphorus atom,<sup>13b, 15</sup> as is the case in the phosphate esters,

$[(\text{RO})_3\text{P}^+-\text{O}^- \longleftrightarrow (\text{RO})_3\text{P}=\text{O}]$ . We conclude, therefore, that the large positive chemical shifts observed in the adducts strongly suggest an oxyphosphorane structure (XIX) rather than an open dipolar structure (XVII). This conclusion is based on the further reasonable assumption that covalent-bond formation between the fifth

(13) (a) J. R. Van Wazer, "Phosphorus and its Compounds," Interscience Publishers, Inc., New York, N. Y., 1938; (b) p. 43; (c) p. 237.

(14) (a) P. C. Lauterbur, in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, Inc., New York, N. Y., 1962, Ch. 7, *cf.* pp. 515–523; (b) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Ch. 12, *cf.* p. 346. Original references are given in these reviews.

(15) J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).

(15a) NOTE ADDED IN PROOF.—The peaks given in Table I were obtained at 16.2 Mc./sec. With the varian HR 100 spectrometer at 40.5 Mc./sec. it was possible to observe, in XI11, the ten lines resulting from a  $\text{P}^{31}$  nucleus in the environment of nine methoxyl protons (measurements by Mr. S. Heller of S. U. of N. Y.).

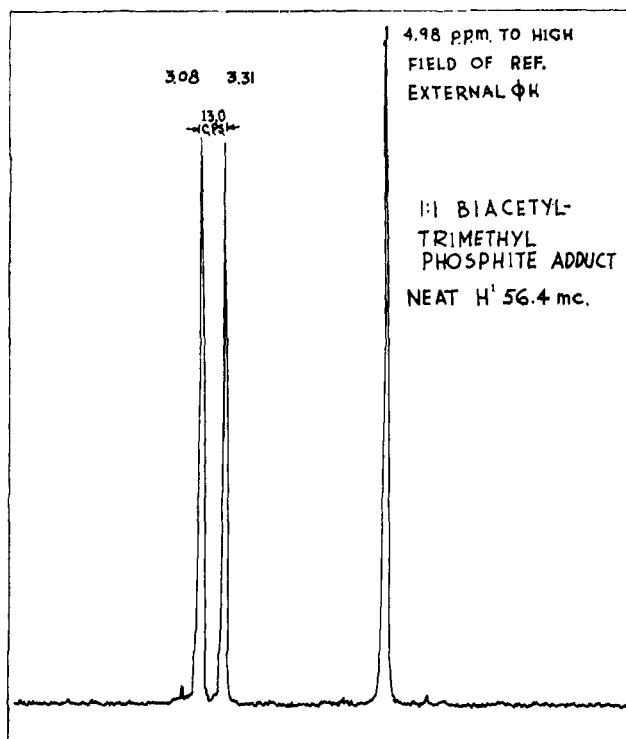


Fig. 2.— $H^1$  n.m.r. spectrum of the pure liquid 1:1 biacetyl-trimethyl phosphite adduct, at 56.4 Mc./sec., relative to benzene as external reference. The spectrum of a 10%  $CCl_4$  soln. was obtained at 60 Mc./sec., relative to cyclohexane as internal reference; the latter was measured in  $CCl_4$  soln. against internal TMS; the shifts are: 6.56  $\tau$  ( $J_{HP} = 13$  c.p.s.) and 8.25  $\tau$ .

oxygen atom of an adduct and the phosphorus of a tetraalkoxyphosphonium cation is an effective way of shielding the  $P^{31}$  nucleus, while a simple approach of the two ends of the charged dipolar ion is not.

It should be noted that the chemical shift of  $PCl_5$  vapor<sup>16</sup> (or  $CS_2$  solution<sup>15</sup>) is strongly positive,  $\delta = +78.6$  p.p.m. at 170°. This is one of the few cases in which there is reasonable evidence for the pentacovalency of phosphorus; the molecules have a trigonal bipyramidal configuration.<sup>13c,17</sup> Another compound in which phosphorus is pentacovalent<sup>13c,17</sup> and in which its chemical shift<sup>16</sup> is positive is  $PF_5$ ,  $\delta = +35$  p.p.m. (in the liquid under pressure).

Further comparisons between the phosphorus chlorides and the phosphorus esters are instructive. In both cases the shielding of the  $P^{31}$  nucleus is relatively low in the triply-connected member of the series. Thus,  $PCl_3$  gives a strongly negative chemical shift,  $\delta = -219$  p.p.m. (compare with phosphite esters). In  $Cl_3PO$ ,  $\delta = -1.9$  p.p.m.; therefore,  $\Delta PO-P = +217$  p.p.m. Again, as in the ester case, the effect of the oxygenation is to produce a large positive shift. The percentage increase in the chemical shift is very similar in the two changes:  $Cl_3P$  to  $Cl_3PO$  and  $(C_2H_5O)_3P$  to  $(C_2H_5O)_3PO$ . If this parallelism were to be maintained, then, from the percentage increase in the shift resulting from the change  $Cl_3P$  to  $PCl_5$ , one would predict a value of  $\delta = +49$  p.p.m. for the oxyphosphoranes, the change here being  $(CH_3O)_3P$  to  $(CH_3O)_3P(OR)_2$ . Table I shows that the chemical shifts of the trialkyl phosphite adducts are very close to this value. Recently, the  $P^{31}$  n.m.r. of crystalline  $PCl_5$  was observed<sup>18</sup> and was

(16) K. Moedritzer, L. Maier, and L. C. D. Groenewegle, *J. Chem. Eng. Data*, **7**, 307 (1962).

(17) D. S. Payne, *Quart. Rev. (London)*, **15**, 173 (1961).

(18) E. R. Andrews, A. Bradbury, R. G. Eades, and G. J. Jenkes, *Nature*, **188**, 1096 (1960).

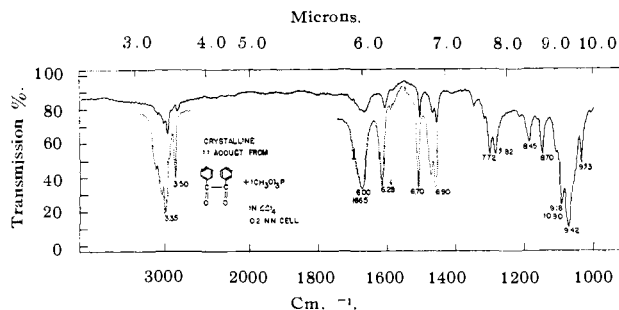


Figure 3.

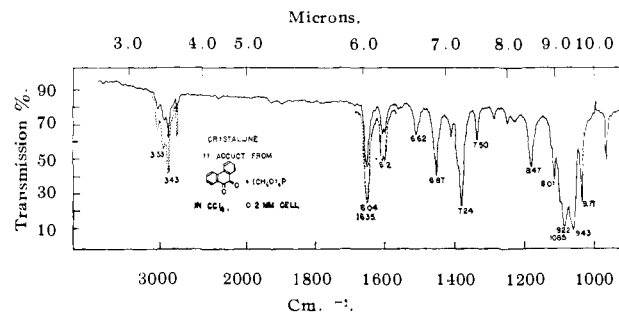


Figure 4.

found to give two signals, one at  $-91$  p.p.m. and the other at  $+281$  p.p.m. These crystals are known<sup>13c,19</sup> to have the units  $[PCl_4]^+$  and  $[PCl_6]^-$ . The  $P^{31}$  chemical shift of  $H[PF_6]$  is strongly positive,<sup>20</sup>  $\delta = +118$  p.p.m.; hence, the signal at  $\delta = -91$  p.p.m. in the chloride is probably due to  $[PCl_4]^+$ . From the percentage increase in the shielding which results when a fourth chlorine atom is added to  $PCl_3$  to form  $[PCl_4]^+X^-$ , one would estimate a value of  $\delta \sim -61$  p.p.m. for a tetraalkoxyphosphonium cation,  $[(C_2H_5O)_3P(OR)]^+Y^-$ , in which a fourth alkoxy group has been added to  $(C_2H_5O)_3P$ .

It must be emphasized that a given structural change in a triply-connected phosphorus compound will affect the  $P^{31}$  magnetic shielding in a manner that depends on the kind of atoms directly bonded to the phosphorus. For example, the shifts<sup>13b,14,15</sup> in the phosphine series are:  $(C_6H_5)_3P$ ,  $\delta = +6$  p.p.m.,  $(C_6H_5)_3PO$ ,  $\delta = -27$  p.p.m.,  $\Delta PO-P = -33$  p.p.m.;  $(C_2H_5)_3P$ ,  $\delta = +20$  p.p.m.,  $(C_2H_5)_3PO$ ,  $\delta = -48$  p.p.m.,  $\Delta PO-P = -68$  p.p.m.<sup>21</sup> These changes ( $\Delta PO-P$ ) are in the opposite direction to the changes in the ester and in the halide series. The behavior<sup>13d,14,15</sup> of the nitrogen compounds,  $(R_2N)_3P$ , and of the sulfur compounds,  $(RS)_3P$ , in this respect ( $\Delta PO-P$  is  $+$ ) parallels the behavior of the esters and the halides.

**Proton N.m.r. Spectrum.**<sup>22</sup>—The spectrum of the pure liquid biacetyl-trimethyl phosphite adduct (XIII) is reproduced in Fig. 2. There are no major impurities. The doublet at low field, with  $J_{HP} = 13$  c.p.s., is due to the  $CH_3OP$  groups, in which the proton line is split by the phosphorus.<sup>14</sup> There is one doublet only; therefore the three methoxyl groups are equivalent or indistinguishable. The singlet at high field is due to the methyl groups attached to carbon; evidently, they are equivalent or indistinguishable. There are in the molecule nine methoxy protons and six methyl protons

(19) D. Clark, H. M. Powell, and A. F. Wells, *J. Chem. Soc.*, 642 (1942).

(20) H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **22**, 162 (1954).

(21) The value<sup>16</sup> of  $\delta = +2.8$  p.p.m. has been recorded for "liquid  $[(CH_3)_3PH][Cl]$ ". One wonders if this positive value is due to the formation of a "double hydrochloride"  $[(CH_3)_3P(H)Cl]_2$ , not much different from  $HPF_6$ .<sup>20</sup>

(22) (a) N.m.r. Spectra Catalog (Spec. No. 67), compiled by N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, Varian Associates, 1962; (b) L. M. Jackman, "Applications of N.m.r. Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 58.

and, consequently, the peak intensities should be in the ratio 3:3:4, as was found to be the case.

The essential features of the spectrum were not altered when the liquid adduct XIII was dissolved in dry carbon tetrachloride. The chemical shifts in the  $\tau$ -scale<sup>22</sup> are: 6.56  $\tau$  ( $J_{HP} = 13$  c.p.s.) and 8.25  $\tau$ . For comparison, the spectrum of trimethyl phosphate was examined in  $CCl_4$  solution; its doublet was at 6.30  $\tau$  ( $J_{HP} = 13$  c.p.s.); *i.e.*, at somewhat lower field than the doublet of the adduct. The methoxyl protons appear therefore to be more shielded in the adduct than in the phosphate ester.

The position of the high-field methyl group (8.25  $\tau$ ) in the adduct is very close to the position of a methyl group attached to a carbon-carbon double bond. For example,<sup>22a</sup> the methyl of 1-chloro-2-methylpropene is at 8.23  $\tau$ , and that of isobutylene<sup>22b</sup> is at 8.30  $\tau$ .

The  $H^1$  n.m.r. spectrum of the adduct (Fig. 2) is compatible with the oxyphosphorane structure (XIXa  $\equiv$  XIII) and possibly favors it over the open dipolar structure XVIIa. It is not evident why the methoxyl protons would be more shielded in the dipolar structure than in trimethyl phosphate, or why the high field methyl protons would be so deshielded. Both of these features, however, are accommodated by the oxyphosphorane formulation. The presence of one doublet due to three methoxyl groups probably means that these methoxyls occupy positions in the molecule which are readily interchangeable. The methoxyls may exchange positions without rupture of a phosphorus-oxygen bond, or, the oxyphosphorane may be in rapid equilibrium with very small amounts of a dipolar structure, for example the open form XVIIa.

**Structure of Other  $\alpha$ -Diketone-Tertiary Phosphite Adducts and *o*-Quinone-Tertiary Phosphite 1:1 Adducts.**—The substances described in Table I have three main features in common: (1) the position and the intensity of the strong infrared band(s) due to the P-O-C (alkyl) stretching vibrations, relative to the same band(s) in the corresponding alkyl phosphate<sup>9b</sup>  $(RO)_3PO$ ; (2) the absence of strong carbonyl absorption in the infrared; (3) the large shift of the  $P^{31}$  n.m.r. signal to high field of the external reference,  $H_3PO_4$ . *These similarities strongly suggest that all the adducts have the same type of cyclic unsaturated oxyphosphorane structure, as shown in Chart I.*

The infrared spectra of the benzil-trimethyl phosphite adduct (X) and of the phenanthrenequinone-trimethyl phosphite adduct (VII) are shown in Fig. 3 and 4, respectively. The C=C stretching vibrations of the aromatic ring can be seen near 6.2  $\mu$  (1610  $cm^{-1}$ ) and 6.7  $\mu$  (1525  $cm^{-1}$ ).<sup>9c</sup> It should be noted, however, that the 1610- $cm^{-1}$  band in Fig. 3 shows no evidence of the 1580- $cm^{-1}$  band which usually appears when a benzene ring is conjugated with an unsaturated group.<sup>9c</sup>

An interesting feature of these spectra is the band at 6.02  $\mu$  (1665  $cm^{-1}$ ) in the benzil adduct and at 6.04  $\mu$  (1655  $cm^{-1}$ ) in the phenanthrenequinone adduct. These bands, although weak, appear to be genuine and not due to carbonyl impurities, since they were observed in a number of preparations, at various concentrations in  $CCl_4$  solution, in a liquid film of the low-melting adduct X, and in a Nujol mull of adduct VII. The intensities relative to the 6.2  $\mu$  band remained unchanged. The adducts can be recrystallized from hexane without appreciable changes. We can only suggest that these bands may be related to the very weak 5.72  $\mu$  band of the biacetyl adduct (Fig. 1). They might be due to C=C bonds in the unsaturated oxyphosphoranes.

Other features of interest in the spectra of this new type of substance can be deduced from the data given

in Table I and in Fig. 1, 3, and 4. (a) The quinone adducts have no absorption in the P=O region<sup>9</sup> at 7.7–8.1  $\mu$  (1300–1230  $cm^{-1}$ ), but the  $\alpha$ -diketone adducts have bands in this region, which could on superficial examination be mistaken for P=O absorption.

(b) The strongest band(s) in the trialkyl phosphite adducts appears near the region of the P-O-C (alkyl) stretching vibrations<sup>9</sup> of the normal alkyl phosphate esters, which is 9.52–10.1  $\mu$  (1050–990  $cm^{-1}$ ). However, this band(s) is significantly lower (*ca.* 0.2–0.3  $\mu$ ) in the adduct than in the corresponding phosphate; for instance, all the *methyl* adducts have two strong bands, one at 9.18–9.22  $\mu$  and the other at 9.30–9.43  $\mu$ , while the strongest band in trimethyl phosphate is at 9.55  $\mu$  (*i.e.*, the frequency increases by about 30–45  $cm^{-1}$ ).

The P-O- $CH_3$  group of a methyl phosphate ester gives rise to a second, much weaker band at 8.47  $\mu$  (1180  $cm^{-1}$ ).<sup>9b</sup> The *methyl* phosphite adducts all have a weak band near 8.45  $\mu$ .

(c) The strongest band in the triphenyl phosphite adducts is very close to the P-O-C (aryl) band in the normal phenyl phosphate esters.<sup>9b</sup> This band is at 8.30  $\mu$  (1250  $cm^{-1}$ ) in IX, at 8.23  $\mu$  in XII, and at 8.33  $\mu$  in triphenyl phosphate.<sup>9b</sup>

The P-O- $C_6H_5$  of triphenyl phosphate has a second, weaker band at 9.71  $\mu$  (1030).<sup>9b</sup> The phenyl adducts also show a weak band at 9.7–9.8  $\mu$ .

(d) Like most phosphate esters,<sup>9c</sup> the adducts have a band near 10.3–10.4  $\mu$  (*ca.* 960  $cm^{-1}$ ); however, this is moderately strong only in the phenyl adducts.

The suggestion that the 1:1 adducts formed from certain tertiary phosphite esters and certain *o*-quinones and  $\alpha$ -diketones have a cyclic unsaturated oxyphosphorane structure does not exclude the possibilities that: (1) a relatively small amount of the open dipolar structure could exist in equilibrium with the cyclic structure, in particular in certain solvents; (2) other phosphite esters or other trivalent phosphorus compounds could form different types of adducts. These studies are being continued.

**Other Studies of the Reactions of Trialkyl Phosphites with  $\alpha$ -Diketones.**—Birum and Dever have reported<sup>23</sup> liquid 1:1 adducts from trialkyl phosphites and  $\alpha$ -diketones. They concluded that the 1:1 adducts had the oxyphosphorane structure. Kukhtin and his co-workers<sup>8a,b,c</sup> have made various contradictory suggestions on the structures of these 1:1 adducts; however, in a very recent publication<sup>8i</sup> they have accepted the *oxyphosphorane*<sup>18</sup> formulation.

## Experimental<sup>24</sup>

The tertiary phosphite esters were purified by prolonged treatment with sodium ribbon, followed by fractional distillation. The carbonyl compounds were freshly distilled or recrystallized from aprotic solvents. Hexane and benzene were dried over sodium. Carbon tetrachloride was dried over  $P_2O_5$  and distilled. All operations were carried in dry  $N_2$ . *Moisture and oxygen must be avoided in making and in handling the 1:1 adducts.*

The 1:1 *o*-quinone-trialkyl phosphite adducts are best prepared by addition of the phosphite to a suspension of the *o*-quinone in benzene at 20°.

The 1:1  $\alpha$ -diketone-trialkyl phosphite adducts are best prepared in the absence of solvents, at 15–60°, using about 10 mole % excess of phosphite or equimolar amounts of the reactants.

The triphenyl phosphite adducts were prepared at 110–120° in an excess of the phosphite as solvent. Only typical procedures are given. The properties of the compounds are listed in Table I and the formulas are gathered in Chart I.

**Trialkyl Phosphite Adducts.** (a) **In Benzene Solution.** Procedure A.—Trimethyl phosphite (6.82 g., 55 mmoles) was

(23) G. H. Birum and J. L. Dever, Abstracts, Div. of Org. Chem., 135th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958, p. 101-P.

(24) Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Micro-Tech Laboratories, Skokie, Ill.

added to a suspension of phenanthrenequinone (10.4 g., 50 mmoles) in dry benzene (100 ml.), under nitrogen with stirring. A clear, red-brown solution was observed after 45 min. at 20°. Within 2 hr., the solution was nearly colorless. Removal of the benzene *in vacuo* left a yellow oil which soon became a nearly colorless crystalline mass (16 g.). One recrystallization from hexane gave the colorless phenanthrenequinone-trimethyl phosphite adduct (VII), m.p. 71–73°, in 90% yield (15 g.). The analytical sample had m.p. 74–75°.

Other trialkyl phosphite adducts were prepared in ca. 95% yield by this method. The reaction with aliphatic  $\alpha$ -diketones, like biacetyl, is particularly exothermic and must be moderated by external cooling.

(b) **In the Absence of Solvents.** Procedure B.—Trimethyl phosphite (6.82 g., 50 mmoles) was mixed with solid benzil (10.5 g., 50 mmoles) under nitrogen. An exothermic reaction ensued, and a colorless oil resulted within 30 min. The oil was dissolved in hexane (30 ml.) and the solution was cooled at 0°. Colorless crystals of the benzil-trimethyl phosphite adduct (X), m.p. 47–49° separated within 8–10 hr.; the yield was nearly quantitative.

Biacetyl (74 g.) was added dropwise to trimethyl phosphite (135 g.) under nitrogen, with stirring and external cooling. The

mixture was then kept at 60° for 15 min. and submitted to fractional distillation. The colorless biacetyl-trimethyl phosphite adduct (XIII) was collected at 45–47° (0.5 mm.); the yield was quantitative. The liquid adduct becomes slightly yellow on standing, or in contact with air, even if the latter is dry, since biacetyl is formed by oxidation.

**Triphenyl Phosphite Adducts.**—A suspension of phenanthrenequinone (2.08 g., 10 mmoles) in triphenyl phosphite (12.4 g., 40 mmoles) was kept 16 hr. at 110°, under nitrogen with stirring. The pale yellow solution was cooled, treated with hexane, and filtered. The colorless insoluble phenanthrenequinone-triphenyl phosphite adduct (IX) (4.5 g.) had m.p. 143–145°. One recrystallization from benzene-hexane gave material of m.p. 145–147°.

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, YALE UNIVERSITY SCHOOL OF MEDICINE, NEW HAVEN 11, CONN.]

## The Participation of the Amide Group in the Solvolysis of Phosphoric Acid Esters. I. Phosphotriesters in Alkaline Media

BY CHRISTINE ZIOUDROU AND GASTON L. SCHMIR

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Phosphotriesters of type I containing a neighboring amide group have been synthesized. Exposure of such triesters to dilute ethoxide or *t*-butoxide solution at room temperature results in the rapid formation of cyclic structures and expulsion of a phosphodiester fragment. Detailed kinetic data and spectrophotometric evidence support the hypothesis that the rate-limiting step of the reaction consists of intramolecular nucleophilic attack of the amide anion on the alkyl carbon, resulting in carbon-oxygen cleavage. The ability of the phosphodiester anion to act as a leaving group is compared to that of other anions. Quantitative measure of the efficiency of the intramolecular process is provided by comparison to the solvolytic behavior of ethyl diphenyl phosphate.

### Introduction

Intramolecular nucleophilic reactions of derivatives of carboxylic acids have received close scrutiny in the past decade because of their possible relevance to the mechanisms of certain enzymatic events.<sup>1</sup> It is less well known that the solvolytic behavior of esters of phosphoric acid is also profoundly influenced by neighboring nucleophilic functions. While there has been sporadic description of phenomena best explained on the basis of intramolecular processes, detailed mechanistic studies have been few and little kinetic information is available. For example, the ease of hydrolysis of *o*-carboxyphenyl dihydrogen phosphate (salicyl phosphate) has been ascribed<sup>2</sup> to participation of the *o*-carboxylate ion. The rapid acid-catalyzed isomerization of phosphomonoesters of 1,2-diols (*e.g.*,  $\alpha$ -glycerophosphate) seems to proceed *via* the formation of an intermediate cyclic diester.<sup>3</sup> Numerous investigations<sup>3b,4</sup> have established that the rate and direction of hydrolysis of phosphodiester is markedly affected by the presence of a vicinal hydroxyl group, whose intervention in the hydrolytic process is responsible, for instance, for the alkaline lability of ribonucleic acids.<sup>5</sup>

Alkaline treatment of phosphotriesters derived from ethanolamine<sup>6</sup> or ethylene glycol<sup>7</sup> affords products whose nature suggests the involvement of the neighboring amino or hydroxyl function in the solvolytic reaction. A recent report has demonstrated that the fast rate of hydrolysis of dimethyl phosphoacetoin<sup>8</sup> in weakly basic solution is a consequence of the presence of an adjacent keto group.

It appeared of interest to examine the effects of another nucleophilic entity upon the solvolysis of phosphoric acid esters. To this end, substances incorporating an *amide* grouping appropriately situated *vis-à-vis* a *phosphotriester* function were studied in alkaline media. The intramolecular interaction of the ionized amide group with the phosphotriester moiety is documented in this communication.

### Results

In preliminary experiments, phosphotriesters of general structure I were exposed to dilute sodium ethoxide or potassium *t*-butoxide at room temperature. Such treatment resulted in rapid, extensive, and irreversible spectral changes in the ultraviolet region (Fig. 1). Repetition of this procedure on a preparative scale (see Table VI, Experimental) resulted in the isolation of cyclic products II (in yields of 70–95%) and of phosphodiester (yields of 50–95%). The  $\Delta^2$ -oxazoline IIa, formed from Ia, Ib, and Id, was shown to be identical

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