

**Kinetics.** The kinetic procedures used were the same as those described in the preceding paper.<sup>4</sup>

**Acetolysis Product Analysis of 3,3-Dimethyl-anti-7-tosyloxybicyclo[2.2.1]heptan-2-one (6).** A solution of 0.50 g of 6 in 20 ml of 0.1 M sodium acetate in acetic acid was sealed in an ampoule and heated in a bath at 200° for 3 hr (ca. 5 half-lives). After cooling to room temperature the ampoule was opened and the contents were poured into 250 ml of water. The acidic solution was neutralized with sodium bicarbonate and extracted with three 150-ml portions of ether. The ethereal extracts were combined and dried over anhydrous magnesium sulfate. Removal of the drying agent by filtration and distillation of the solvent gave a residue which on short-path distillation gave 0.16 g (67%) of a colorless liquid which was clearly identified as a carboxylic acid by its infrared spectrum.<sup>17</sup> Vpc analysis on a 3% FFAP on Chromosorb G column showed this acid to be greater than 95% pure. Nmr spectroscopy showed this acid to be ( $\Delta$ -2-cyclopentenyl)dimethylacetic acid (23). An analytical sample was obtained by preparative vpc on a 5 ft  $\times$   $\frac{3}{8}$  in. 5% SE-30 on Firebrick column.

*Anal.* Calcd for  $C_9H_{14}O_2$ : C, 70.13; H, 9.09. Found: C, 70.16; H, 9.17.

Vpc analysis of the reaction mixture after 10 min at 200° (ca.

5% reaction) showed the same product composition as obtained at the completion of the reaction. That 23 was not arising from the decomposition of either 16 or 21 under the reaction conditions was shown by separate control experiments in which 16 and 21 were subjected to the reaction conditions for 30 min at 200°. Relatively little decomposition of 16 or 21 occurred during the 30-min period. However, on prolonged heating at 200°, 16 and 21 did decrease in quantity.

**Product Analysis of the Acetolysis Mixture from 3,3-Dimethyl-anti-7-tosyloxybicyclo[2.2.1]heptan-2-one.** Because of the instability of 16 and 21 to the reaction conditions employed in the acetolysis of 7, the product determination could not be made at the conclusion of the reaction. A solution of 0.051 g of 7 in 2 ml of 0.1 M sodium acetate buffered glacial acetic acid was sealed in a solvolysis tube and heated to 200° for 30 min ( $t_{1/2}$ , 760 min at 200°). After cooling to room temperature the solution was poured into 40 ml of water and neutralized with 5 g of sodium bicarbonate. The neutralized solution was extracted with two 20-ml portions of ether and the combined extracts were dried over anhydrous magnesium sulfate. Removal of the drying agent and solvent gave a liquid residue. Vpc analysis showed the solvolysis mixture to consist of 50% 16, 20% 21, and ten other components which constituted the remaining 30%. The identity of the two major components was established by comparison of vpc retention times on three columns with different liquid phases (PDEAS, XF-1150, and FFAP).

**Acknowledgment.** We are indebted to the Petroleum Research Fund administered by the American Chemical Society for a grant which supported this work.

(17) It is interesting to note that this carboxylic acid could be readily extracted from sodium bicarbonate solution which had completely neutralized the acetic acid solvent. The crude product, prior to distillation, corresponded to a quantitative yield of 23. Sodium hydroxide solution neutralized 23. In addition 23 was readily converted to its methyl ester with diazomethane. We wish to acknowledge the assistance of Dr. Richard Steppel in the identification of 23.

## The Peroxide Route to Pentaoxyphosphoranes<sup>1</sup>

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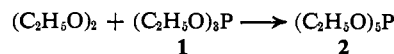
Contribution from the School of Chemistry, Rutgers University, New Brunswick, New Jersey 08903. Received March 22, 1969

**Abstract:** A variety of pentaoxyphosphoranes have been prepared by allowing trisubstituted phosphites to react with diethyl peroxide. In one case the same pentaoxyphosphorane was prepared by condensation of  $\beta$ -naphthoquinone and triethyl phosphite and by reaction of the phosphite, 3, with diethyl peroxide. The relative rates of formation of the pentaoxyphosphoranes have been obtained as a function of structure. Decomposition of five-membered ring containing pentaoxyphosphoranes gives epoxides in a stereospecific process.

The syntheses of the first pentaoxyphosphoranes were reported nearly simultaneously in 1958 by Birum and Dever<sup>3</sup> and Kukhtin.<sup>4</sup> These compounds were prepared by condensation of  $\alpha$ -dicarbonyl compounds with trisubstituted phosphites. Since that time Ramirez and coworkers have conducted extensive studies of this method of producing these and related substances.<sup>5</sup> Their preparation has been reviewed.<sup>6</sup>

Other reviews on the structures and properties of penta-coordinated compounds have appeared in the recent literature.<sup>7</sup>

In 1964, Denney and Relles<sup>8a</sup> found that diethyl peroxide and triethyl phosphite reacted to give a substance which was characterized as pentaethoxyphosphorane (2). Subsequently pentamethoxyphosphorane and an



oxyphosphorane containing a six-membered ring were prepared by the phosphite-peroxide reaction.<sup>8b</sup>

(1) This research has been supported in part by the National Institutes of Health under GM-12625.

(2) National Institutes of Health Predoctoral Fellow, 1965-1968.

(3) G. H. Birum and J. L. Dever, Abstracts, 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1958, p 101-P.

(4) V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, 121, 466 (1958).

(5) (a) F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, 82, 2652 (1960); (b) F. Ramirez and N. B. Desai, *ibid.*, 85, 3252 (1963); (c) F. Ramirez in "Organophosphorus Compounds," International Symposium, Heidelberg, 1964, IUPAC, Butterworth and Co., Ltd., London, 1964, pp 337-369; (d) F. Ramirez and N. Ramanathan, *J. Org. Chem.*, 26, 3041 (1961); (e) F. Ramirez, N. Ramanathan, and N. B. Desai, *J. Am. Chem. Soc.*, 85, 3465 (1963); (f) F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, 84, 1317 (1962); (g) F. Ramirez, A. V. Patwardhan, N. B. Desai, N. Ramanathan, and C. V. Greco, *ibid.*, 85, 3056 (1963); (h) F. Ramirez, A. V. Patwardhan, N. Ramanathan, N. B. Desai, C. V. Greco, and S. R. Heller, *ibid.*, 87, 549 (1965); (i) F. Ramirez, S. B. Bhatia, and C. P. Smith, *Tetrahedron*, 23, 2067 (1967);

(j) F. Ramirez, S. B. Bhatia, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, 32, 2194 (1967); (k) F. Ramirez, M. Nagabhushanam, and C. P. Smith, *Tetrahedron*, 24, 1785 (1968).

(6) (a) L. D. Quin in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, Chapter 3; (b) F. Ramirez, *Accounts Chem. Res.*, 1, 168 (1968).

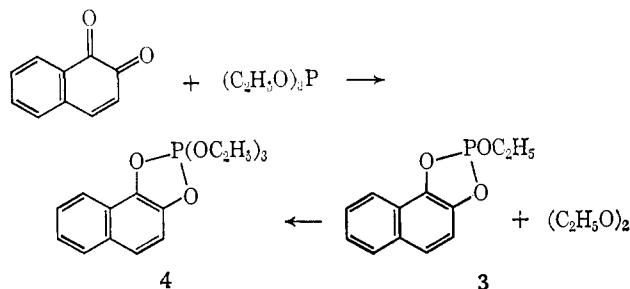
(7) (a) E. L. Muetterties and R. A. Schunn, *Quart. Rev. (London)*, 20, 245 (1960); (b) R. J. Gillespie, *Angew. Chem. Intern. Ed.*, 6, 819 (1967); (c) F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968).

(8) (a) D. B. Denney and H. M. Relles, *J. Am. Chem. Soc.*, 86, 3897 (1964); (b) D. B. Denney and S. T. D. Gough, *ibid.*, 87, 138 (1965).

The objectives of this work were to prepare a variety of oxyphosphoranes by the peroxide-phosphite reaction, to evaluate the variables which influence the reactions course and to prepare the same oxyphosphorane by the  $\alpha$ -dicarbonyl condensation reaction and by the peroxide-phosphite reaction. During the course of this work the decomposition of some five-membered saturated rings containing oxyphosphoranes has been studied.

## Results

Condensation of  $\beta$ -naphthoquinone with triethyl phosphite followed the usual course and gave the oxyphosphorane **4** in excellent yield. The same oxyphosphorane was produced when the phosphite **3** was allowed to



react with diethyl peroxide. The product from this reaction was considerably less pure than that from the condensation reaction. Nevertheless **4** was the major component formed from **3** and diethyl peroxide. The characterization of **4** rests in the main on its  $^{31}\text{P}$  nmr spectrum which shows an absorption at +45 ppm relative to 85% phosphoric acid as an external standard. Ramirez<sup>5c</sup> has discussed the importance of  $^{31}\text{P}$  nmr spectroscopy as a means of identifying oxyphosphoranes. Pentaalkoxyphosphoranes containing one unsaturated five-membered ring absorb around +50. For example the condensation product of phenanthrenequinone and triisopropyl phosphite absorbs at +48.6.

The  $^1\text{H}$  nmr spectrum of **4** has a triplet at 1.22 ( $J_{\text{HH}} = 7$  Hz), each line of which is split into a doublet ( $J_{\text{PH}} = 2$  Hz). The absorption is due to the methyls of the ethoxy group. The coupling between the methyls and phosphorus appears to be characteristic for pentaalkoxyphosphoranes which contain ethoxy groups. The methylene protons absorb at 4.05 and appear as an approximate quintet which in reality is the result of two overlapping quartets ( $J_{\text{PH}} = J_{\text{HH}} = 7$  Hz). The aromatic protons absorb at 7.43 (complex multiplet).

These data indicate that the phosphite-peroxide reaction does give the same material as the carbonyl condensation reaction. They also indicate that the condensation reaction is much more specific.

The phosphite-peroxide reaction is potentially a much more general route to oxyphosphoranes than is the carbonyl condensation reaction. Previous studies<sup>8</sup> have indicated, however, that the reaction yields phosphate(s) as well as the oxyphosphoranes. Previous attempts to separate the oxyphosphoranes from the phosphates(s) have never yielded a phosphate free product. It was decided therefore to study the preparation of pentaalkoxyphosphorane with the hopes of finding conditions which would yield a minimum amount of triethyl phosphate. The results of this study are collected in Table II (see Experimental Section). In general it has been

found that the best yields of pentaalkoxyphosphorane are obtained when diethyl peroxide and triethyl phosphite are allowed to react in a mole ratio of 1.5:1 at room temperature. It has been found that degassing the reaction mixture also improves the quality of the product. Typically after 20 days the product mixture contains some unreacted phosphite, 10%, triethyl phosphate, 15%, and pentaalkoxyphosphorane, 75%. Evacuation of the reaction mixture concentrates triethyl phosphate and pentaalkoxyphosphorane. Attempts to separate these two substances by distillation under a variety of conditions has led in some cases to partial separation. Triethyl phosphate and pentaalkoxyphosphorane can be separated quite efficiently by extracting the reaction mixture after evacuation with one-half to three-quarters of a volume of propylene carbonate. Triethyl phosphate is very soluble in propylene carbonate while pentaalkoxyphosphorane is not. This procedure yields pentaalkoxyphosphorane which is contaminated with a small amount of propylene carbonate. Detailed studies on the thermal and hydrolytic stability of pentaalkoxyphosphorane have not been conducted. It has been found to be stable for weeks in a refrigerator and can be handled under normal atmospheric conditions without difficulty.<sup>9</sup> Pentaalkoxyphosphorane shows five equivalent ethoxy groups in its  $^1\text{H}$  nmr spectrum at 100 MHz. The equivalency is probably due to intramolecular pseudorotation.<sup>6b,7c</sup> The  $^1\text{H}$  nmr spectrum at  $-60^\circ$  shows that the ethoxy groups are still equivalent. Studies at lower temperatures are in progress.

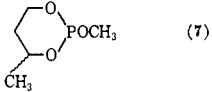
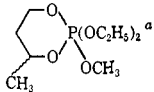
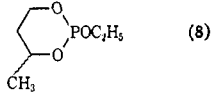
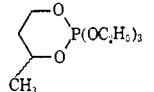
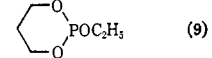
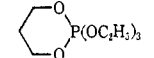
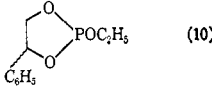
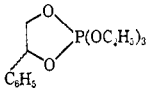
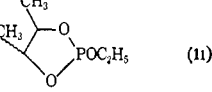
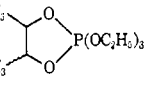
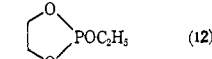
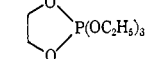
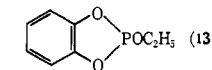
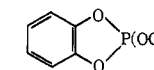
A variety of trisubstituted phosphites have been allowed to react with diethyl peroxide. The formation of pentaalkoxyphosphoranes has been demonstrated in the main by  $^{31}\text{P}$  nmr studies. The  $^1\text{H}$  nmr spectra are also in agreement with the formation of pentaalkoxyphosphoranes as the major products. In all cases phosphates were produced as minor products. Table I contains the  $^{31}\text{P}$  chemical shifts of the starting phosphites and the pentaalkoxyphosphoranes. The phosphite, **13**, reacted most rapidly of those studied, with saturated five-membered ring phosphites being the next most reactive. The six-membered ring and acyclic phosphites were of essentially the same reactivity. The difference in reactivity is not large with **13** being about seven times more reactive than the six-membered ring and acyclic phosphites. Triphenyl phosphite did not react with diethyl peroxide to give a pentaalkoxyphosphorane when they were allowed to stand at room temperature for 40 days.

Reaction of the tetramethyl-substituted five-membered ring phosphite, **14**, with diethyl peroxide yielded an intermediate oxyphosphorane **15**, which decomposed at room temperature to give tetramethylethylene oxide and triethyl phosphate.<sup>10</sup> The phosphorane from **10** was stable at room temperature but decomposed on pyrolysis at  $120^\circ$  for 17 hr with the formation of styrene oxide and triethyl phosphate. Decomposition of a mixture by heating at  $117^\circ$  for 42 hr of phosphoranes prepared from a mixture of phosphites 88% *dl*, **11**, and

(9) One of the most important uses of pentaalkoxyphosphorane is as a precursor to other pentaalkoxyphosphoranes by alcohol exchange and thus a considerable amount of attention has been devoted to its preparation and purification.

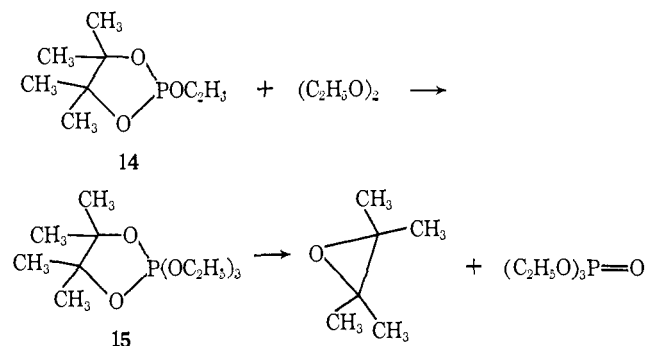
(10) These experiments were performed by Dr. D. Z. Denney.

Table I.  $^{31}\text{P}$  Nmr Chemical Shifts of Oxyphosphoranes

Compound		$^{31}\text{P}$ chemical shifts	
Phosphite(s)	Oxyphosphorane	Phosphite(s)	Oxyphosphorane
$(\text{CH}_3\text{O})_3\text{P}$ (5)	$(\text{CH}_3\text{O})_3\text{P}(\text{OC}_2\text{H}_5)_2^a$	-141	+68
$((\text{CH}_3)_2\text{CHO})_3\text{P}$ (6)	$((\text{CH}_3)_2\text{CHO})_3\text{P}(\text{OC}_2\text{H}_5)_2^a$	-138	+73
 (7)		-131, -132	+71
 (8)		-128	+71
 (9)		-132	+72
 (10)		-135, -139	+53
 (11)		<i>dl</i> -140, <i>meso</i> -135	+56
 (12)		-135	+52
 (13)		-125	+50

<sup>a</sup> Mixtures of oxyphosphoranes may have been present in these cases.

12% *meso*, 11, gave 85% *cis*-2-butene oxide and 15% *trans*-2-butene oxide.



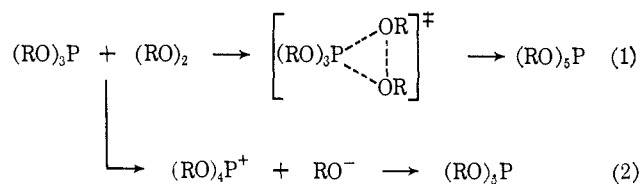
## Discussion

The preparation of 4, by both the condensation of the quinone with triethyl phosphite and by reaction of the phosphite, 3, with diethyl peroxide, clearly demonstrates that pentaoxyphosphoranes are formed by the latter reaction. Unfortunately conditions have not yet been found which allow the production of oxyphosphoranes by the peroxide-phosphite reaction without the production of phosphate(s). It is, however, the only general route available for the production of these substances and thus it is receiving continued study.

The  $^{31}\text{P}$  nmr spectra of the pentaoxyphosphoranes show that those substances with one five-membered ring absorb at lower fields than those containing a six-membered ring or no ring at all. The pattern seems to be quite general and no exceptions have been found as yet. The  $^1\text{H}$  nmr spectra of all of the pentaoxyphosphoranes show complete equivalency of the methylene

and methyl absorptions of the ethoxy groups. Equivalency is undoubtedly due to pseudorotation which is occurring rapidly on the nmr time scale.<sup>7</sup>

The mechanism of the production of oxyphosphoranes by the phosphite-peroxide reaction is unknown. Two general possibilities exist. They are direct formation *via* a transition state in which there is bonding to both oxygens by phosphorus and the pentaoxyphosphorane is formed in one step, eq 1. The second in-



volves displacement on oxygen to give a tetraalkoxyphosphonium alkoxide which then reacts to give the pentaoxyphosphorane, eq 2. Displacement reactions in which phosphites are the nucleophiles have not been studied extensively so that the effect of structure on reactivity has not been put on as firm a basis as it should be. Aksnes and Erikson<sup>11</sup> have shown that the order of reactivity for several phosphites with ethyl iodide is isopropyl phosphite > triethyl phosphite > six-membered ring phosphite > five-membered ring phosphite. The total difference in reactivity was a factor of 10. Litt<sup>12</sup> has studied the rates of condensation of a variety of phosphites with biacetyl. He found the same order of reactivity and also noted that the phosphite, 13, was very unreactive relative to the other phosphites. Varga<sup>13</sup>

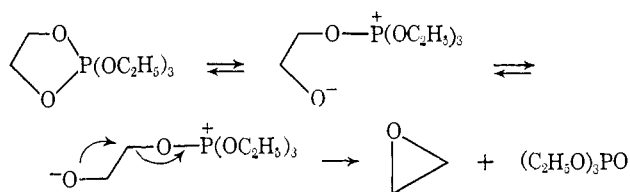
(11) G. Aksnes and R. Erikson, *Acta Chem. Scand.*, **20**, 2463 (1966).

(12) A. Litt, Ph.D. Thesis, Rutgers University, 1968.

(13) S. Varga, Ph.D. Thesis, Rutgers University, 1968.

found the same order of reactivity for the reactions of phosphites with benzoyl peroxide. It is important to note that the relative rate order found in this present study is opposite to that observed in the other studies. In particular the unusual reactivity of **13** should be noted. These data may suggest that direct formation of the pentaoxyphosphorane is the correct mechanism. Such a route would lead to a transition state in which relief of strain in the five-membered ring compounds would be occurring and this might account for the reactivity of **13** and the other five-membered ring compounds. Clearly though these data provide no more than an indication of mechanism.

The stereochemistries of the decompositions of the five-membered ring containing oxyphosphoranes suggest a mechanism in which a ring P-O bond is cleaved followed by rotation and displacement of triethyl phosphite.



A similar decomposition of aryl-substituted five-membered ring oxyphosphoranes has been recorded.<sup>14</sup>

### Experimental Section<sup>15</sup>

**Phosphites.** The phosphites were prepared by standard procedures. Their <sup>1</sup>H nmr spectra and other physical properties can be found in the thesis of D. H. Jones, Rutgers, University, 1969.

**Preparation of 2-Ethoxy[1,2-*d*]naphtho-1,3,2-dioxaphosphole (**3**).** Freshly distilled phosphorus trichloride, 13.2 g (0.0960 mol), in a few milliliters of ether was added in one portion to a stirred solution of β-naphthohydroquinone, 10.0 g (0.0697 mol), in 60 ml of ether to which one drop of water had been added. Within 1 hr a white precipitate had formed. Tetrahydrofuran was added and the reaction mixture was heated under reflux, 44°, for 26 hr. Nitrogen was bubbled through the homogeneous reaction mixture and then the remaining solvent was distilled to give a cream solid.

The solid was dissolved in dry benzene and the resulting solution was cooled in an ice bath. A solution of absolute ethanol, 2.88 g (0.0626 mol), and pyridine, 4.94 g (0.0625 mol), in a few milliliters of benzene was added dropwise to the stirred benzene solution. The mixture was filtered after stirring at room temperature for 30 min. The solvent was removed and the residue was distilled, bp 111–116° (0.11 mm), to give 9.0 g (61.%) of the desired phosphite.

The <sup>1</sup>H nmr spectrum had a triplet at 1.05 (*J*<sub>HH</sub> = 7 Hz, -CH<sub>3</sub>), multiplet at 3.48 (*J*<sub>PH</sub> = *J*<sub>HH</sub> = 7 Hz, -CH<sub>2</sub>-) and aromatic absorptions at 7.36. Glpc (6 ft 10% silicone gum rubber SE-30, 195°, 75 ml/min) showed one major component >95% with a retention time of 4.8 min. The <sup>31</sup>P nmr spectrum had one absorption at -123.

*Anal.* Calcd for C<sub>2</sub>H<sub>11</sub>O<sub>3</sub>P: C, 61.50; H, 4.73. Found: C, 61.68; H, 4.71.

(14) F. Ramirez, A. S. Gulati, and C. P. Smith, *J. Org. Chem.*, **33**, 13 (1968).

(15) All <sup>1</sup>H nmr spectra were run on a Varian Model A-60 spectrometer unless otherwise noted. All chemical shifts are reported in parts per million relative to tetramethylsilane, 0.0 ppm. All <sup>31</sup>P nmr spectra were recorded with a Varian Model HA-100 operating at 40.5 MHz. Phosphorus shifts are reported in parts per million from external 85% phosphoric acid. Routine infrared spectra were recorded on either Perkin-Elmer Model 137 or Beckmann Model IR5A spectrometers. Other infrared spectra were run on a Perkin-Elmer Model 21 spectrometer. Gas-liquid partition chromatographic analyses were performed on an F & M Model 700 gas chromatograph unless otherwise specified. Conditions used during glpc analyses are specified in the text as follows: column description, column temperature, helium flow in milliliters per minute. Analyses were performed by G. Robertson, Florham Park, N. J. Melting points were determined on a "Mel-Temp" apparatus and are uncorrected.

**Preparation of **4** by Reaction of **3** with Diethyl Peroxide.** Diethyl peroxide, 0.2779 g (3.09 mmol), was added to 0.6510 g (2.78 mmol), of **3** at -78°. The mixture was maintained in the cooling bath for 1 hr. The cooling bath was allowed to warm during this period. The mixture was then transferred to an ice bath which was allowed to warm to room temperature. The reaction mixture was investigated by <sup>1</sup>H and <sup>31</sup>P nmr spectroscopy at various intervals. The major product had an absorption at +45 in the <sup>31</sup>P nmr spectrum. Other small absorptions were found at -131, -129, *ca.* +1, +17, and +22.

This reaction was conducted several times with similar results. Attempts to isolate **4** by distillation led to decomposition and no separation. The <sup>1</sup>H nmr spectrum of the reaction mixtures were in accord with **4** being present as the major product; however, it is quite clear that other substances are formed during the reaction.

**Preparation of **4** by Reaction of β-Naphthoquinone with Triethyl Phosphite.** Triethyl phosphite, 1.66 g (0.010 mol), was added dropwise to a cooled suspension under nitrogen of 1.58 g (0.010 mol) of β-naphthoquinone in 20 ml of benzene. The mixture was stirred for 2 hr. The solvent was removed under reduced pressure to give a dark brown oil a portion of which was distilled (7 × 10<sup>-5</sup> mm, block 110–115°). The <sup>1</sup>H nmr spectrum of this material had a triplet at 1.22 (*J*<sub>HH</sub> = 7 Hz, -CH<sub>3</sub>), each line of which was further split into a doublet (*J*<sub>PH</sub> = 2 Hz). A multiplet was present at 4.05 and absorptions for aromatic hydrogens were also found. The ratio of areas was 9:6:5.9. The <sup>31</sup>P nmr spectrum had one absorption at +45.

**Reaction of Triethyl Phosphite (**1**) with Diethyl Peroxide.** Diethyl peroxide was prepared according to the method of Nangia and Benson.<sup>16</sup> Attempts to modify their isolation procedure always gave poor yields of impure diethyl peroxide. The results of five reactions under different conditions and with different samples of peroxide are reported below. In runs A–D the samples of diethyl peroxide and triethyl phosphite were placed in separate tubes on a high-vacuum line. Each sample was degassed by freezing and pumping to 5 × 10<sup>-5</sup> mm. The peroxide was then allowed to distill into the phosphite; the mixture was degassed and the tube was sealed. The course of the reaction was followed by <sup>31</sup>P nmr spectroscopy. The peroxide used in runs A and B was isolated by merely distilling it from the anisole extracts obtained during the Nangia and Benson procedure. The diethyl peroxide used in run C was added to triphenyl phosphite in a mole ratio of 2.5:1; after 8 days the diethyl peroxide was distilled from the reaction mixture. In run D the diethyl peroxide was isolated according to the procedure of Nangia and Benson. In run E the triethyl phosphite and diethyl peroxide were mixed in an nmr tube which was then capped with a plastic cap. The peroxide was from the same batch as used in runs A and B. The results of these experiments are collected in Table II.

Table II. Reactions of Diethyl Peroxide with Triethyl Phosphite

Run	Ra-tio <sup>a</sup>	Component	Day									
			2	3	5	6	7	12	20	26	48	
A	1.18	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P			61	40	35		10	4		
		(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> PO		8	13	15		20	26			
		(C <sub>2</sub> H <sub>5</sub> O) <sub>5</sub> P		31	47	50		70	70			
		(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P		45	29	10		0	0			
B	2.32	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> PO		22	23	29		34	42			
		(C <sub>2</sub> H <sub>5</sub> O) <sub>5</sub> P		36	48	61		66	58			
		(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P	68	60		40			11			
		(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> PO	6	7		8			14			
C	1.29	(C <sub>2</sub> H <sub>5</sub> O) <sub>5</sub> P	26	33		52			75			
		(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P		46		20						
		(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> PO		14		19						
		(C <sub>2</sub> H <sub>5</sub> O) <sub>5</sub> P		40		61						
D	1.94	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P			53	44	29		9			
		(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> PO		16		20	22		28			
		(C <sub>2</sub> H <sub>5</sub> O) <sub>5</sub> P		29		36	49		63			
		(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P										
E	1.18	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P										
		(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> PO										
		(C <sub>2</sub> H <sub>5</sub> O) <sub>5</sub> P										
		(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P										

<sup>a</sup> Mole ratio of diethyl peroxide to triethyl phosphite. <sup>b</sup> The percentage of each component was determined by peak height measurements of the <sup>31</sup>P nmr signals. This procedure probably gives a minimum value for the major component.

(16) P. Nangia and S. W. Benson, *J. Org. Chem.*, **27**, 1882 (1962).

**Preparation and Isolation of Pentaethoxyphosphorane.** Diethyl peroxide, 13.22 g (0.146 mol), was added to 17.49 g (0.105 mol) of triethyl phosphite in a 100-ml round-bottomed flask fitted with a gas-inlet tube. The mixture was cooled to  $-70^\circ$  and then evacuated to *ca.* 1 mm. Argon was admitted to the system and it was evacuated again. This procedure was repeated. The gas-inlet tube was closed and the vessel was stored in the dark at room temperature. After 20 days the  $^{31}\text{P}$  nmr spectrum indicated that there was present 72.5% pentaethoxyphosphorane, 19.4% triethyl phosphate, and 8.1% triethyl phosphite. The reaction mixture was evacuated slowly with stirring to *ca.* 1 mm. After 20 hr of stirring *in vacuo* the  $^{31}\text{P}$  nmr spectrum showed there was 79.6% pentaethoxyphosphorane, 18.6% triethyl phosphate, and 2.2% triethyl phosphite present in the residue. In a typical experiment the yield of pentaethoxyphosphorane at this point was 57%. Further purification was conveniently effected by extracting the pentaethoxyphosphorane with propylene carbonate. Treatment of the mixture of pentaethoxyphosphorane and triethyl phosphate, two volumes, with propylene carbonate, one volume, followed by separation of the layers and  $^{31}\text{P}$  nmr investigation showed that the pentaethoxyphosphorane was essentially free of triethyl phosphate and that the propylene carbonate contained triethyl phosphate and pentaethoxyphosphorane in a 2:1 ratio. Small amounts of propylene carbonate were found by glpc analysis in the pentaethoxyphosphorane. The  $^1\text{H}$  nmr spectrum ( $\text{CDCl}_3$ ) recorded at 100 MHz on a sample of pentaethoxyphosphorane purified by the extraction procedure had a triplet at 1.14 ( $J_{\text{HH}} = 7$  Hz) each line of which was split into a doublet ( $J_{\text{PH}} = 2$  Hz). There was also an apparent quintet centered at 3.8 but which in reality is two overlapping quartets ( $J_{\text{HH}} = 7$  Hz and  $J_{\text{PH}} = 7$  Hz). Essentially no other lines were present.

**Relative Reactivities of Phosphites with Diethyl Peroxide.** The phosphites **3**, **5**, **6**, **7** (mixture of isomers whose ratio was *ca.* 95:5), **8** (mixture of isomers, *ca.* 95:5), **10** (mixture of isomers 63:37), **11** (mixture of isomers *dl* 86%, total *meso* 14%), **9** and **13** were allowed to react with diethyl peroxide in nmr tubes. The phosphites **5**, **6**, **8**, **10**, and **13** were allowed to react with diethyl peroxide in the mole ratio of 1.21, 1.32, 1.18, 1.02, and 1.26, respectively, in sealed degassed nmr tubes. The phosphites **7**, **10**, **11**, **13**, and triphenyl phosphite were allowed to react with diethyl peroxide in the mole ratios of 1.21, 2.00, 1.04, 1.13, and 1.12, respectively, in nmr tubes which were closed with plastic caps.

The mixture of phosphites, **7**, yielded after 9 days, 58% unreacted phosphite, 11% cyclic phosphates, 10% acyclic phosphates, and 21% oxyphosphorane. The phosphite, **8**, yielded 63% oxyphosphorane after 48 days. After 15 days, **10** reacted to give 60% oxyphosphorane and **11** yielded 51% oxyphosphorane. The phosphite, **13**, was the most reactive; after 1 day 42% oxyphosphorane was present and after 6 days 64% was formed. The phosphites **5** and **6** yielded 65 and 61% oxyphosphoranes after 22 days.<sup>17</sup>

**Products from the Reactions of **5** and **6** with Diethyl Peroxide.** The reaction mixtures from the experiments reported above were examined by glpc to determine the composition of the decomposition products. The sealed nmr tubes were carefully opened and the volatiles were removed *in vacuo*. The residue from the diethyl peroxide-trimethyl phosphite reaction was analyzed by glpc (6 ft 10% silicone gum rubber SE-30, 82°, 100 ml/min). Four major components were observed. The first and last appear to be trimethyl phosphate and triethyl phosphate, respectively. Each of these peaks was augmented when authentic samples were added to the reaction mixture and reinvestigated by glpc. It is assumed that the other components are dimethyl ethyl phosphate and diethyl methyl phosphate. An estimate of the composition of the mixture by the peak height times half-width procedure indicated that there was 16% trimethyl phosphate, 29% dimethyl ethyl phosphate, 36% methyl diethyl phosphate, and 18% triethyl phosphate present in the reaction mixture.

Glpc analysis of the triisopropyl phosphite-diethyl peroxide reaction mixture (6 ft Ucon W-98, 110°, 100 ml/min) showed that triethyl phosphate comprised less than 4% of the reaction mixture. The distribution of products was not reproducible on repeated injections. Four components were always found in the chromatogram in the region where the four possible phosphates would be expected to appear.

**Reaction of **11** with Diethyl Peroxide.** Diethyl peroxide, 2.825 g (0.03135 mol), was added to 4.925 g (0.030 mol) of **11**, 87% *dl*,

and 13% *meso* isomers. After 15 days, the mixture was evacuated to *ca.* 1 mm and the volatile material was condensed in a liquid nitrogen trap. The infrared spectrum of the volatile material had a broad hydroxyl absorption at 3.0  $\mu$  and a  $-\text{OO}-$  band at 11.4  $\mu$ . The  $^1\text{H}$  nmr spectrum had absorptions at 1.15 (triplet,  $J = 7$  Hz), 3.54 (quartet  $J = 7$  Hz), 3.89 (quartet,  $J = 7$  Hz) and 4.09. Glpc analysis (5.0 ft silicone gum rubber, 27°) showed that diethyl peroxide and ethanol were the major components. Glpc analysis (16 ft 5% silicone gum GE-XE-60, 135°, 45 ml/min) showed components at 1.28 min (unidentified), 1.64 min (phosphites), 4.20 min (triethyl phosphate), 5.24 min (small, unidentified), and 20.7 min (cyclic phosphates).

The experiment was repeated. The residue remaining after removing the volatiles *in vacuo* was shown to contain by  $^{31}\text{P}$  nmr spectroscopy 4% cyclic phosphates, 20% acyclic phosphate, and 76% oxyphosphoranes.

**Pyrolysis of the Mixture of *meso*- and *dl*-4,5-Dimethyl-2,2,2-triethoxy-1,3,2-dioxaphospholanes.** The nonvolatile residue obtained in the second experiment reported above was heated in a sealed tube at 117° for 42 hr. The  $^{31}\text{P}$  nmr spectrum of the pyrolysate showed that it contained 3% cyclic phosphates and 97% triethyl phosphate. The  $^1\text{H}$  nmr spectrum of the pyrolysate had absorptions characteristic of those found for triethyl phosphate. An absorption at 2.80 was also found. An authentic sample of *cis*-2,3-epoxybutane had an absorption at 2.80. The coupling patterns were identical. Additional small absorptions centered at 2.53 were identical in pattern with those found in an authentic sample of *trans*-2,3-epoxybutane. The integrated spectrum indicated that there was 13–15% of the *trans*-epoxide present.

Glpc analysis (50 ft silicone rubber SE-30, 25°, 50 ml/min) of the pyrolysis product gave peaks at 9.6 and 11.7 min. These peaks were identified as *trans*- and *cis*-2-butene oxides by comparison of retention times with those of authentic samples. The peak for the *cis*-2-butene oxide was augmented with an authentic sample. The ratio of *trans*-oxide/*cis*-oxide was 15/85. Glpc analyses on a 16 ft silicone gum GE-SE-60 (125°, 17 ml/min) gave both epoxides at 1.3 min, a trace of phosphite at 1.7 min, major component, triethyl phosphate at 3.5 min, and a small amount of cyclic phosphates at 14.2 min.

**Pyrolysis of 4-Phenyl-2,2,2-triethoxy-1,3,2-dioxaphospholane.** A mixture containing 17% 4-phenyl-2-ethoxy-1,3,2-dioxaphospholane, 16% triethyl phosphate, and 65% of the oxyphosphorane was pyrolyzed in a sealed tube for 17 hr at 120°. The  $^{31}\text{P}$  nmr spectrum after the pyrolysis showed that the composition was 10% phosphite, 3% cyclic phosphates, and 87% triethyl phosphate. Styrene oxide was shown to be the other major product by augmentation of its glpc peak (6 ft Ucon and 16 ft GE-XE-60), with authentic material.

**Reaction of 3,3,4,4-Tetramethyl-2-ethoxy-1,3,2-dioxaphospholane (**14**) with Diethyl Peroxide.** To 1.92 g (0.01 mol) of **14** cooled in an ice bath was added dropwise 0.90 g (0.01 mol) of diethyl peroxide. The reaction mixture was allowed to warm to room temperature and then it was stored in the dark. The progress of the reaction was monitored by following the  $^1\text{H}$  and  $^{31}\text{P}$  nmr spectra on an aliquot of the mixture. One day after mixing the  $^{31}\text{P}$  nmr spectrum had three absorptions at  $-151$ , starting phosphite,  $-11.6$ , cyclic phosphate, and an absorption at  $+60$ . Three days after mixing the  $+60$  absorption had disappeared and a new one was present at  $+1.1$ . Three days later the  $^{31}\text{P}$  nmr spectrum was no longer changing. It showed absorption at  $-150$  (11%),  $-11.9$  (29%), and  $+1.1$  (60%).

The  $^1\text{H}$  nmr spectrum of the reaction mixture after 4 days had a strong single absorption at 1.22 as well as complex multiplets at 4.0 and 1.2.

Another reaction mixture was allowed to stand for 4 weeks. The volatile products were evaporated at room temperature and 5 mm. The distillate, 1.0 g, was collected at  $-78^\circ$ . The  $^1\text{H}$  nmr spectrum had a single sharp absorption at 1.23. There were small absorptions at 1.1, 3.5, and 3.9. Glpc analysis (16 ft GE-XE-60, 72°) gave five components with retention times of 1.4, 1.8, 2.7, 3.0, and 4.0 min. The major component had a retention time of 3.0 min.

An authentic sample of 2,3-epoxy-2,3-dimethylbutane was prepared.<sup>18</sup> The  $^1\text{H}$  nmr spectrum had a single absorption at 1.23. Small amounts of impurities were also present. Glpc analyses of a mixture of authentic 2,3-epoxy-2,3-dimethylbutane and the distillate from the reaction mixture gave a chromatogram in which the major component had been augmented.

(17) Full details of these experiments can be found in the thesis of D. H. Jones, Rutgers University, 1969.

(18) J. D. C. Wilson, II, U. S. Patent 2,838,524 (1958); *Chem. Abstr.*, **52**, 20195 (1958).