

Oxyphosphoranes

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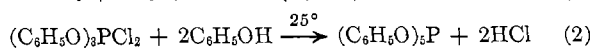
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X-Ray analysis and variable-temperature ^1H and ^{31}P nmr spectrometry have elucidated the stereochemistry of five-membered cyclic oxyphosphoranes. Compounds with P-N and P-C bonds in addition to P-O bonds are discussed. The phosphorus is at the center of a trigonal bipyramid and the ring is in an apical-equatorial plane. The bipyramid is crowded due to several short intramolecular nonbonded distances. Positional exchange among the groups can occur by pseudo-rotation (intramolecular bond-bending) and by P-O bond fission, depending on temperature. Stereoisomeric oxyphosphoranes differing in configuration at the phosphorus can be prepared. The stability of oxyphosphoranes, the barrier to pseudo-rotation, and the positions taken by the groups on the bipyramid depend on electronegativity and on steric requirements of the groups.

Pentaoxyphosphoranes, $(\text{RO})_5\text{P}$, are ortho esters of phosphoric acid. They are important substances because they contribute a new dimension to the chemistry of the biologically indispensable phosphate esters, $(\text{RO})_3\text{PO}$, and because they lend themselves very well to the study of problems of structure and of stereochemistry associated with the pentavalent state of phosphorus. The replacement of oxygen by nitrogen and by carbon in the oxyphosphoranes leads to interesting families of compounds, $(\text{RO})_{5-n}\text{P}(\text{NR}_2)_n$ and $(\text{RO})_{5-n}\text{PR}_n$, $n = 0-4$. Much can be learned about pentavalent phosphorus from the differences in physical and chemical properties among compounds in these series and in the series of pentaarylphosphoranes and halophosphoranes. This account sets forth some of the main results that have been obtained in this laboratory during the past 3 years. We have summarized previous research in this field.¹ The pentaarylphosphoranes² and the halophosphoranes,³ which cannot be discussed here for lack of space, have been the subject of recent reviews.

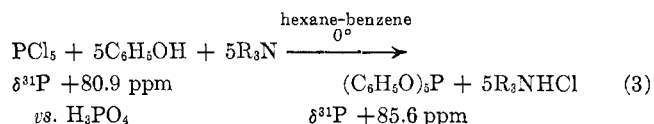
I. Pentaoxyphosphoranes from Phosphorus Pentachloride

The first report of the preparation of a pentaoxyphosphorane appeared⁴ in 1927 and was said to have been confirmed⁵ in 1959. The reported synthesis of pentaphenoxyphosphorane is shown in eq 1 and 2.



A reinvestigation⁶ of these reactions showed conclusively that, as described, they could not have pro-

duced the pentaoxyphosphorane. The latter can be made from PCl_5 and phenol in the presence of a tertiary amine, as shown in eq 3.



The main argument in favor of the pentacovalency of the phosphorus in pentaphenoxyphosphorane is the large positive value of the ^{31}P nmr shift, which proved to be very close to that of PCl_5 itself, both in CH_2Cl_2 solution. This point will be discussed in a subsequent section.

Pentaphenoxyphosphorane was converted into dichlorotriphenoxyphosphorane by HCl , even under very mild conditions. Further replacements of phenoxy groups by chlorines were not observed. The reaction of pentaphenoxyphosphorane (**1**) with 1 equiv of catechol in CH_2Cl_2 at 25° produced the catecholtriphenoxyphosphorane **2**. A second mole of catechol led to the spirodicatcholphenoxyphosphorane **3**. Evidently, the introduction of five-membered rings in the oxyphosphoranes enhanced their stability. The presence of the rings resulted in a significant lowering of the positive values of the ^{31}P nmr shifts. The configuration assigned to these compounds is based on data presented below.

The availability of authentic samples of these pentaoxyphosphoranes, **1**, **2**, and **3**, enabled us to show that previously described procedures⁴ for their syntheses were in error. The rather complex chemistry associated with the reactions of phenol and of catechol with PCl_5 and with dichlorotriphenoxyphosphorane^{4,5} has now been clarified.⁶

II. Oxyphosphoranes from the Reactions of Trivalent Phosphorus Compounds with Carbonyl Functions

It has been shown¹ that the phosphorus atom of trialkyl phosphites becomes attached to the carbonyl oxygen of *p*-quinones (**4**). The first product of this reaction is a dipolar ion, **5**, which undergoes a rapid alkyl group translocation leading to the alkyl ether of a *p*-quinol phosphate, **6**.

(1) (a) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); (b) F. Ramirez, *Bull. Soc. Chim. France*, 2443 (1966).

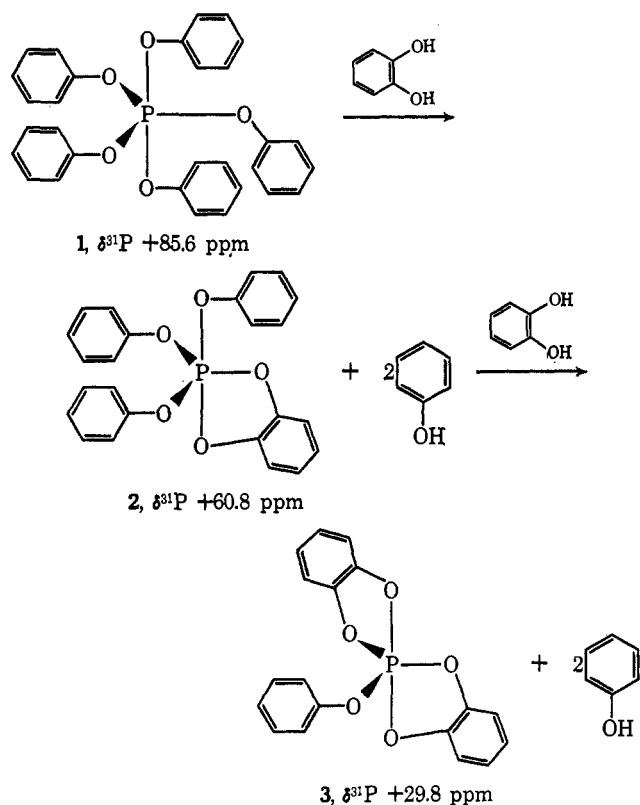
(2) (a) G. Wittig, *ibid.*, 1162 (1966); (b) D. Hellwinkel, *Ber.*, **99**, 3660 (1966).

(3) (a) E. L. Muettterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966); (b) R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965); (c) D. S. Payne, "Topics in Phosphorus Chemistry," Vol. 4, Interscience Publishers, Inc., New York, N. Y., 1967.

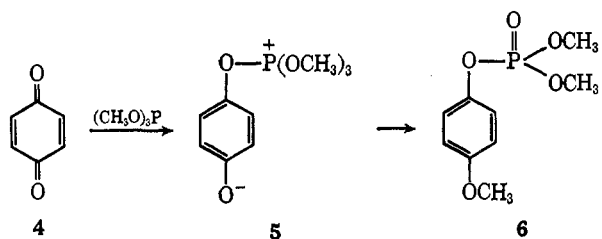
(4) L. Anschutz, H. Boedeker, W. Broecker, and F. Wenger, *Ann.*, **454**, 71 (1927).

(5) I. N. Zhmurova and A. V. Kirsanov, *J. Gen. Chem. USSR*, **29**, 1668 (1959).

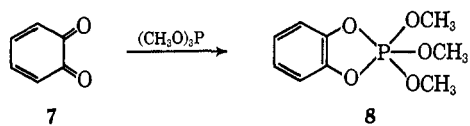
(6) F. Ramirez, A. J. Bigler, and C. P. Smith, submitted for publication.



This property of the trialkyl phosphites can be adapted to the synthesis of a wide variety of five-membered cyclic pentaoxyphosphoranes. Thus, the reaction of the trialkyl phosphites with *o*-quinones

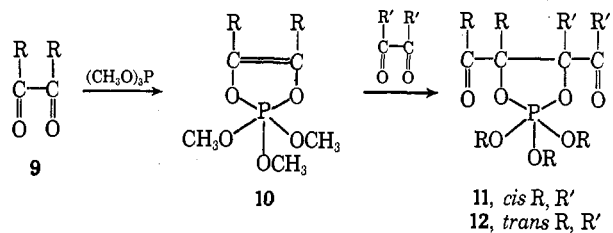


(7) results in the formation of the oxyphosphoranes **8** in high yields and under very mild conditions.¹ When cyclic phosphite esters are employed, spirocyclic phosphoranes analogous to **3** are obtained. Phosphonite and phosphinite esters, $(\text{RO})_2\text{PR}$ and $(\text{RO})\text{PR}_2$, can be used to give cyclic members of the series $(\text{RO})_{5-n}\text{PR}_n$, where $n = 1$ or 2 . The use of tertiary phosphines, R_3P , in this reaction is more limited, but some cyclic dioxaphosphoranes can be made in this way ($n = 3$).⁷ Other α -dicarbonyl compounds behave like the *o*-quinones toward trialkyl phosphites.¹



The unsaturated oxyphosphoranes, e.g., **10**, are derivatives of the 2,2-dihydro-1,3,2-dioxaphospholene ring system. They have the useful property of com-

binning with a second molecule of other mono- and polycarbonyl compounds. This opens a convenient route to derivatives of the 2,2-dihydro-1,3,2-dioxaphospholane ring system, **11** and **12**. This is, in fact, a new approach to the creation of carbon-carbon single bonds in polyoxygenated compounds.⁸



With some α -diketones and many α -keto esters, the second step of this condensation is faster than the first one; in those cases one isolates only the 2:1 adducts, **11** and **12**.

The reaction of trialkyl phosphites with suitably activated monocarbonyl compounds leads directly to the 2:1 adducts, the 1,3,2-dioxaphospholanes.⁹ This happens with *o*- and *p*-nitrobenzaldehydes,⁹ phthalaldehydes,⁸ hexafluoroacetone,⁷ and fluorenone,¹⁰ which yield the oxyphosphoranes **13** and **14**, respectively. In these cases, the substituents around the carbonyl group stabilize the negative charge that develops on the carbonyl carbon during the formation of the 1:1 adduct $(\text{CH}_3\text{O})_3\text{P}^+\text{OC}^-\text{HR}$. In contrast, unsubstituted aliphatic monoaldehydes yield derivatives of the 2,2-dihydro-1,4,2-dioxaphospholane ring systems, **15**, in reactions with trialkyl phosphites.¹ There is no reason for the development of negative charge on carbonyl carbon; the phosphite adds to carbonyl carbon and gives the 1:1 adduct $(\text{CH}_3\text{O})_3\text{P}^+\text{C}(\text{O}^-)\text{HR}$ with the negative charge on oxygen. This type of adduct adds to the second carbonyl compound in the usual way to yield **15**. We have been able to show, using the activated aromatic aldehyde pentafluorobenzaldehyde, that the 1,4,2-dioxaphospholane **16** is the initial product of the reaction with the trialkyl phosphite.¹¹ This oxyphosphorane isomerizes slowly to the 1,3,2-dioxaphospholane **17**. The exact mechanism of this important transformation is not known. Moreover, we have no compelling evidence for assuming that all the 1,3,2-dioxaphospholanes which have been obtained from the reactions of trialkyl phosphites with activated monoketones and with α -dicarbonyl compounds in general involve also a 1,4,2-dioxaphospholane as an unstable precursor.

The assignment of a structure with pentavalent phosphorus to the 1:1 adducts derived from the reactions of trialkyl phosphites with *o*-quinones and with

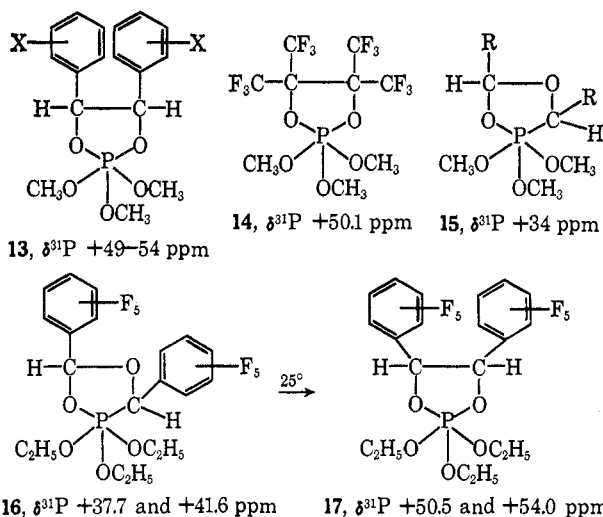
(8) (a) F. Ramirez, S. B. Bhatia, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **32**, 3547, 2194 (1967); (b) F. Ramirez, S. B. Bhatia, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 3030, 3026 (1967).

(9) F. Ramirez, S. B., Bhatia, and C. P. Smith, *Tetrahedron*, **23**, 2067 (1967).

(10) (a) F. Ramirez and C. P. Smith, *Chem. Commun.*, 662 (1967); (b) I. J. Borowitz and M. Ansel, *Tetrahedron Letters*, 1517 (1967); (c) N. P. Gambaryan, Yu. A. Cheburkov, and I. L. Knunyants, *Bull. Acad. Sci. USSR*, **8**, 1433 (1964).

(11) F. Ramirez, A. S. Gulati, and C. P. Smith, unpublished.

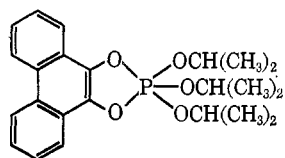
(7) (a) F. Ramirez, M. Nagabhushanam, and C. P. Smith, *Tetrahedron*, **24**, 1785 (1968); (b) F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, *Tetrahedron Letters*, 2151 (1966).



α -diketones was initially based on the large positive value of the ^{31}P nmr shift relative to that of H_3PO_4 . This was done, independently, by Birum and Dever and by Ramirez and Desai, as discussed in our previous reviews on this subject.¹ A third group of investigators led by Kukhtin reported also on the reactions of phosphites with α -diketones; this work has been summarized.¹ Infrared and Raman spectra were utilized in the early studies of the oxyphosphoranes; these data supported, but did not demonstrate conclusively, the phosphorane structure of many of the adducts in solutions and in the solid state.¹ Section III is devoted to the elucidation of the structure of one of the α -quinone-trialkyl phosphite adducts based on the work of Hamilton, *et al.*, at the Brookhaven National Laboratories.¹²

III. Stereochemistry of the Oxyphosphoranes by X-Ray Crystallography

Two allotropic forms of the phenanthrenequinone-triisopropyl phosphite adduct (18) were investigated by single-crystal X-ray diffraction techniques.¹² Some of the results are given in Table I. The phospholene



18, $\delta^{31}\text{P}$ +486 ppm vs. H_3PO_4

ring is in an apical-equatorial plane of a trigonal bipyramid. The apical P–O bonds are longer than the corresponding equatorial P–O bonds. This is attributed to the different character of the σ bonding. The apical P–O bond of the phospholene ring is longer than the apical P–O bond of the alkoxy group. Likewise, the equatorial P–O bond of the ring is longer than the equatorial P–O bond of the alkoxy groups. This is regarded as a manifestation of $\text{pd}-\pi$ bonding. The

(12) (a) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 2268 (1967); (b) R. D. Spratley, W. C. Hamilton, and J. Ladell, *ibid.*, **89**, 2272 (1967).

Table I
Some Bond Lengths and Angles in the
Phenanthrenequinone–Triisopropyl Phosphite Adduct

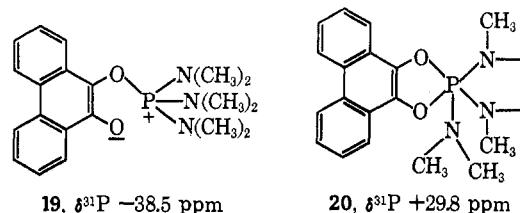
Bond length, Å	Bond angle, deg			
	P–O ₁	O ₁ –P–O ₂	89.3	P–O ₁ –C ₁
P–O ₃	O ₃ –P–O ₂	88.6	P–O ₂ –C ₂	114.2
P–O ₂	O ₃ –P–O ₄	91.3	P–O ₃ –C ₃	121.8
P–O ₄	O ₃ –P–O ₅	93.1	P–O ₄ –C ₄	129.8
P–O ₅	O ₂ –P–O ₄	117.2	P–O ₅ –C ₅	127.5
O ₁ –C ₁	O ₄ –P–O ₅	117.2		
O ₂ –C ₂	O ₅ –P–O ₂	125.5		
C ₁ –C ₂	O ₁ –C ₁ –C ₂	113.9		
O ₃ –C ₃	O ₂ –C ₂ –C ₁	110.3		

phenanthrene ring competes with the phosphorus for the π -bonding electrons of the oxygens which are not available to produce a shortening of the P–O bond of the ring, as is the case in the alkoxy groups.

Two observations are of the utmost importance for an understanding of the factors that affect the stereochemistry of the oxyphosphoranes. (1) The O–P–O and the P–O–C bond angles are capable of rather large distortions (*cf.* Table I). (2) The trigonal bipyramid is crowded due to several short nonbonded distances. The apical oxygen of the ring, O₁, is very close (2.63 Å) to the carbon attached to the equatorial oxygen, C₄. Likewise, the apical oxygen of the alkoxy group, O₃, is very close (2.70 Å) to the carbon attached to the other equatorial oxygen, C₅. Other short distances are: C₃–O₂ = 2.74 Å and C₃–O₄ = 2.86 Å.

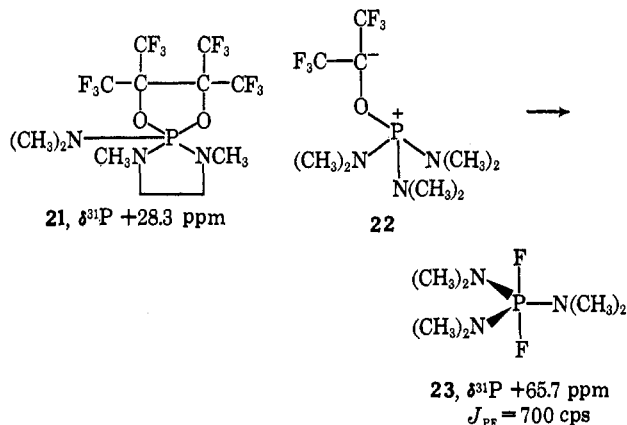
The crowding in the trigonal bipyramid accounts for the greater stability of five-membered cyclic pentaoxyphosphoranes when compared to acyclic pentaoxyphosphoranes.

The remarkable differences in the structures of the 1:1 adducts made from the reaction of carbonyl compounds with acyclic and with five-membered cyclic tris(dialkylamino)phosphines are easily explained in terms of these steric effects.¹³ The adduct made from phenanthrenequinone and tris(dimethylamino)phosphine is an open dipolar ion, **19**, in the crystal and in solutions. The adduct made from the same quinone and a cyclic aminophosphine is an oxyphosphorane, **20**.



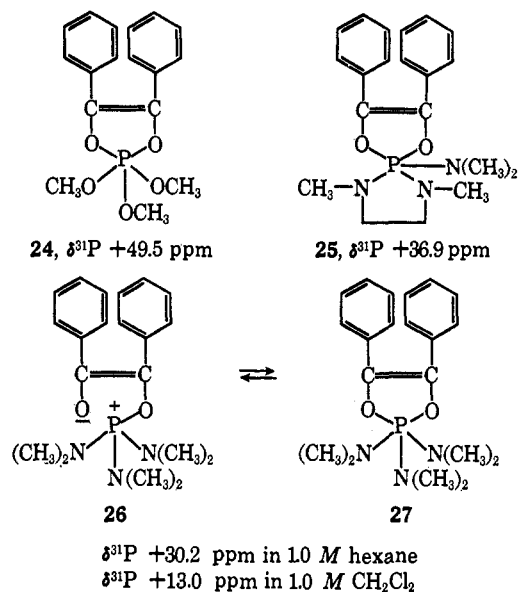
(13) (a) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *ibid.*, **89**, 6283, 6276 (1967); (b) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron*, **24**, 2275 (1968); (c) F. Ramirez, A. S. Gulati, and C. P. Smith, *J. Org. Chem.*, **33**, 13 (1968).

The reaction of hexafluoroacetone with a cyclic aminophosphine gives a stable oxyphosphorane, **21**. The reaction of the same ketone with tris(dimethylamino)phosphine gives a variety of products of molecular fragmentations, among them the fluoroamino-phosphorane **23**. The 2:1 adduct in this case cannot achieve stabilization by formation of an oxyphosphorane analogous to **21**. Molecular rearrangements and fragmentations occur at the stage of the 1:1 adduct **22**.

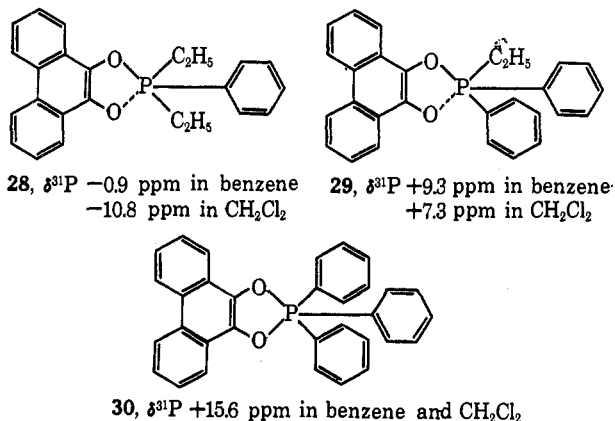


Many puzzling reactions of trivalent phosphorus compounds with carbonyl functions become understandable if one takes into account the influence of steric factors on the stability of oxyphosphoranes and the effect that this has on the over-all course of the reaction. A second important factor is the electronegativity of the elements attached to the phosphorus. Compare the tendency of phosphite to give stable oxyphosphoranes (**8**, **11**, **13**, **14**, and **18**) and the reluctance of the acyclic triaminophosphines to do so; cf. **19** and **22**. This is due in part to the lower electronegativity of the nitrogen and in part to the larger steric requirements of the dialkylamino groups *vs.* the alkoxy groups. These effects can be illustrated with the α -diketone, benzil. Its adduct with trimethyl phosphite is a very stable oxyphosphorane. Its adduct with a five-membered cyclic aminophosphine is a somewhat less stable oxyphosphorane, **25**. Its adduct with tris(dimethylamino)phosphine can be isolated in two crystalline forms; the metastable one is the open dipolar ion **26**, and the stable one is the oxyphosphorane **27**. In solutions both structures are in equilibrium with each other. This equilibrium is rapid relative to the time scale of the nmr phenomenon. Since the dipolar ion has a negative shift and the phosphorane has a positive shift, the observed value is the average of the two. The nature of the solvent affects the position of the equilibrium and hence the value of the shift.

The solvent dependence of the ^{31}P nmr shift is very useful in elucidating the structure of oxyphosphoranes. Note the solvent dependence of the shifts in the adducts **28** and **29** made from phenanthrenequinone and diethylphenylphosphine and ethyldiphenylphosphine.¹⁴



These shifts suggest that in solutions these adducts exist as an equilibrium between oxyphosphoranes and dipolar ions. The adduct of the quinone with triphenylphosphine, **30**, can be made with difficulty,^{7b} but its positive ^{31}P nmr shift is the same in benzene and methylene chloride, suggesting the oxyphosphorane structure.



IV. Stereochemistry of Oxyphosphoranes in Solutions

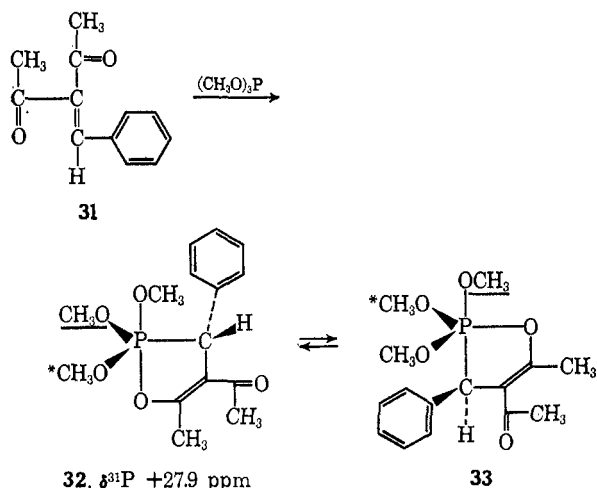
The question of the valency of the phosphorus in a compound suspected of being an oxyphosphorane can be settled by a combination of X-ray crystallography and ^{31}P nmr and infrared spectrometry. However, the elucidation of the stereochemistry of oxyphosphoranes in solution is a more subtle problem due to the positional exchange which may occur under those conditions. The best tools in this type of investigation are variable-temperature ^1H and ^{31}P nmr. The following conclusions have emerged from these studies.

Pentaoxyphosphoranes. A number of oxyphosphoranes of types **8**, **10**, and **24** have been examined in the range -60 to $+30^\circ$. In all cases, the three methoxy groups attached to the phosphorus give only one doublet in the ^1H nmr spectrum.⁷ The doublet is due to H-P coupling. The data suggest that the methoxy groups are undergoing positional exchange among

(14) F. Ramirez, A. S. Gulati, and C. P. Smith, unpublished.

apical and equatorial positions. The exchange may occur by the mechanisms discussed in the next section.

Oxyphosphoranes with One, Two, and Three P-C Bonds. Cyclic tetraoxyalkylphosphoranes, **32**, can be made from trialkyl phosphites and 3-benzylidene-2,4-pentanedione (BPD)¹⁵ (**31**).



The preferred configuration of the trimethyl phosphite adduct is assumed to be **32** from the data of section III and because the element with the lowest electronegativity, carbon, should tend to occupy an equatorial position.³ The ¹H nmr of **32** at -65° is shown in Figure 1 and the numerical data are given in Table II. The three methoxy groups are clearly different; *i.e.*, the trigonal bipyramid is "frozen" in the time scale of the nmr phenomenon. The spectrum at -40° shows evidence of positional exchange among methoxy groups. Note that at $+14^\circ$ (and at $+25^\circ$) there is only one doublet due to these groups.¹⁵

These observations are explained by a mechanism first discussed by Berry¹⁶ in 1960. He pointed out that the groups in apical and equatorial positions of a trigonal bipyramid can exchange places readily by an intramolecular bond-bending which he called *pseudo-rotation*. When this mechanism is applied to **32**, using

Table II

¹H Nmr Data for Methoxy Groups in Equatorial (E) and Apical (A) Positions of Oxyphosphoranes^a

	(CH ₃ O) ₃ P	(CH ₃ O) ₂ PC ₆ H ₅	CH ₃ OP(C ₆ H ₅) ₂
τ_E	6.47; 6.30	6.22; 6.10	None
J_E	12.7; 14.0	12.8; 13.6	None
τ_A	6.61	7.03; 7.03	7.37
J_A	10.6	10.4; 10.4	10.3
τ_{EA}	6.53	6.80; 6.58	None
J_{EA}	12.3	11.5; 11.5	None

^a Adducts from the reaction of 3-benzylidene-2,4-pentanedione with (CH₃O)₃P, (CH₃O)₂PC₆H₅, and CH₃OP(C₆H₅)₂. τ in parts per million *vs.* TMS = 10; J_{HOP} in cycles per second. Solvent: CDCl₃.

(15) (a) F. Ramirez, O. P. Madan, and S. R. Heller, *J. Am. Chem. Soc.*, **87**, 731 (1965); (b) F. Ramirez, J. F. Pilot, O. P. Madan, and C. P. Smith, *ibid.*, **90**, 1275 (1968); (c) F. Ramirez, J. F. Pilot, and C. P. Smith, *Tetrahedron*, in press; F. Ramirez, *Trans. N. Y. Acad. Sci.*, in press.
(16) S. R. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

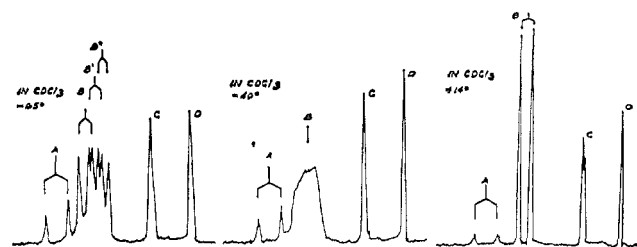


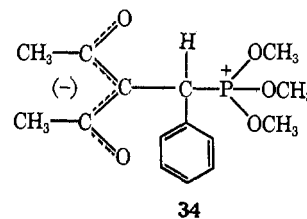
Figure 1. Temperature dependence of the ¹H nmr spectrum of the 3-benzylidene-2,4-pentanedione-trimethyl phosphite adduct: signal A, benzylic ¹H; signals B, B', B'', CH₃O groups; signal C, CH₃CO on phospholene ring; signal D, CH₃ on phospholene ring.

the front-equatorial methoxyl group (*CH₃O) as *pivot*, the new bipyramid **33** is obtained.¹⁷ Note that in **33** the phospholene carbon is in an apical position. This is unfavorable not only on electronegativity grounds³ but also because the short intramolecular nonbonded distances discussed in section III result in considerable steric interference of the groups in the bipyramid. This accounts for the appearance of a barrier to pseudo-rotation which is sufficiently high to permit observation of the three different methoxy groups at -65° .

If the ring carbon of **32** is used as pivot in the pseudo-rotation, that carbon remains in an equatorial position; however, the C-P-O angle in the unsaturated ring must be expanded from 90 to 120°. The energetic consequences of such an expansion are not obvious at this time, but they could contribute to the appearance of the barrier to pseudo-rotation.

Similar observations have been published by Gorenstein and Westheimer¹⁸ while our investigations were in progress.

The ¹H nmr signals due to the acetyl and the methyl groups attached to the phospholene ring of **32** coalesce into one signal at about $+155^\circ$. This change is reversible and is due to an opening of the ring to form the dipolar ion **34**. The coalescence temperature of the corresponding signals in the analog of **32** made from triethyl phosphite is 135°, which shows an interesting relationship between structure and stability in the oxyphosphoranes. Evidently, positional exchange of



(17) To effect one pseudo-rotation in Berry's mechanism, select the front equatorial methoxy group as *pivot* and fix the bipyramid at that point. Push back the two apical groups to close the O-P-O angle from 180 to 120°. Simultaneously, pull forward the two equatorial groups (other than the fixed pivot) to open the O-P-C angle from 120 to 180°. In the new bipyramid, the pivot group remains in an equatorial position, but the other four groups exchange positions. For representational purposes, it is very convenient to reorient the new bipyramid in space as shown in **33**. To arrive at **33**, the new bipyramid was rotated about the pivot axis, 90° counterclockwise, then it was turned upside down, *i.e.*, rotated about the axis of the P-O(ring) bond by 180°.

(18) (a) D. G. Gorenstein and F. H. Westheimer, *J. Am. Chem. Soc.*, **89**, 2762 (1967); (b) D. G. Gorenstein and F. H. Westheimer, *Proc. Natl. Acad. Sci. U. S. A.*, **58**, 1747 (1967); *cf.* also F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

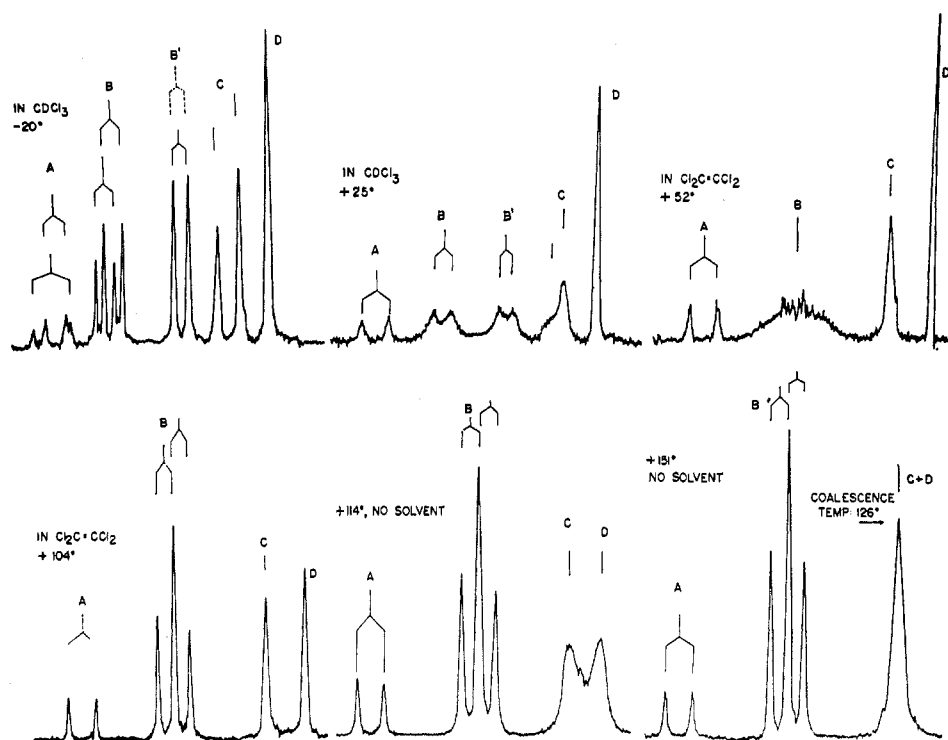


Figure 2. Temperature dependence of the ^1H nmr spectrum of the 3-benzylidene-2,4-pentanedione-dimethyl phenylphosphonite adduct. At -20° : two diastereomers differing in configuration at phosphorus; signals A due to benzylic ^1H ; signals B due to equatorial CH_3O groups of two isomers; signal B' due to apical CH_3O groups of two isomers, not resolved; signals C due to CH_3CO on phospholene for two isomers; signal D due to CH_3 on phospholene for two isomers, not resolved. At $+25^\circ$: two diastereomers at phosphorus; CH_3O groups exchange positions in each isomer. At $+52^\circ$: stereomutation of isomers. At $+104^\circ$ and $+114^\circ$; dipolar ion and phosphorane in equilibrium. At $+151^\circ$: dipolar ion; signal C + D is due to one type of CH_3C group.

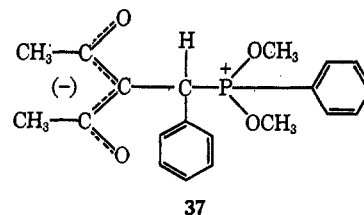
the groups on the trigonal bipyramid can occur by a bond-fission mechanism above certain temperatures. The analogy of this situation with that noted among the oxyaminophosphoranes **26** and **27** is evident.¹³

The reaction of dimethyl phenylphosphonite with BPD gives two diastereomeric oxyphosphoranes, **35** and **36**, which differ in the configuration at the phosphorus. Each diastereomer consists of a pair of enantiomers. In solution at $+25^\circ$, each diastereomer gives a positive ^{31}P nmr signal. The ^1H nmr spectrum of a mixture of **35** and **36** is shown in Figure 2; the corresponding numerical data are given in Table II.

The bipyramids **35** and **36** are "frozen" below -20° . Although the ^1H signals of the two equatorial CH_3O groups are observable, the apical ones cannot be resolved. At about 0° , positional exchange among CH_3O groups of each isomer is noted, but there is no isomerization of **35** into **36**. The spectrum is similar up to $+40^\circ$, but at $\sim +50^\circ$ isomerization is noted. These observations are accommodated by the pseudo-

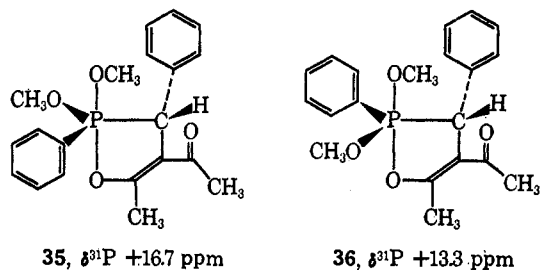
rotation mechanism of Berry. Note that one pseudo-rotation of **35** using the $\text{C}_6\text{H}_5\text{-P}$ bond as pivot places the ring carbon in an apical position, exchanges the CH_3O groups, but leaves the phenyl ring in an equatorial position.¹⁷ This does not result in conversion of **35** into **36**. A second pseudo-rotation places a phenyl on an apical position; two additional pseudo-rotations are required to convert **35** into **36** in this manner. The choice of the ring carbon as pivot requires the expansion of the ring C-P-O angle from 90 to 120° and the placement of a phenyl on an apical position, simultaneously.¹⁵

Above 70° , the P-O bond of the ring of **35** and **36** breaks. This leads to an equilibrium with the dipolar ion **37**. The signals due to the acetyl and the methyl



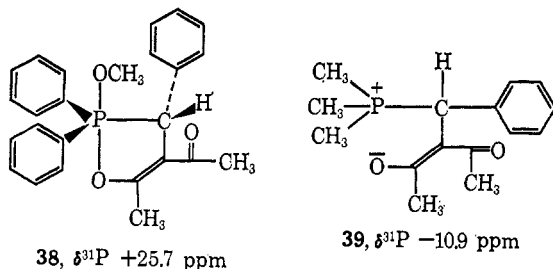
groups coalesce at about $+125^\circ$. Note the spectrum at $+151^\circ$. These changes are reversible. The coalescence temperature of the triethyl phosphite adduct is about 20° lower.¹⁵

The adduct **38** made from methyl diphenylphosphinite and BPD provides the first example of an oxyphosphorane



in which all positional exchanges are frozen in solution at room temperature.¹⁵ The adduct is produced in one configuration only. Its ¹H nmr does not change from -60 to +30°. The data of Table II show that the methoxy is in an apical position. The ¹H nmr spectrum in *o*-dichlorobenzene does not change from +30 to +100°. However, the signals due to the acetyl and the methyl groups coalesce at +127°; *i.e.*, the phosphorane becomes an open dipolar adduct.

The adducts made from trialkyl phosphines and BPD do not form oxyphosphoranes. These adducts are open dipolar ions, **39**, from -40 to +30°. The necessity



of closing the oxyphosphorane ring with the simultaneous placement of carbon atoms in three equatorial positions and one apical position prevents the establishment of the pentacovalency of the phosphorus in this system.¹⁵

V. Conclusions

General methods are now available to make oxyphosphoranes. However, new ones are desirable. An interesting one has been introduced by Denney, *et al.*,¹⁹ and consists of the oxidation of trialkyl phos-

(19) (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).

phites by dialkyl peroxides. They have reported the value $\delta^{31}\text{P}$ +70.7 ppm for the rather unstable $(\text{C}_2\text{H}_5\text{O})_5\text{P}$.

Considerable information is now available on the molecular structure of the oxyphosphoranes and the oxyaminophosphoranes. Further work should define better the electronic and the steric factors that determine the configuration of these compounds and the barrier for the positional exchange of the groups attached to the phosphorus. More X-ray data are very desirable.

One of the most interesting aspects of oxyphosphorane chemistry is that of hydrolyses and alcoholyses.²⁰ In particular, there are striking analogies between these phenomena and related ones in the ordinary phosphate esters. Considerable work has been carried out with the five-membered cyclic oxyphosphoranes and the corresponding phosphate esters. This has resulted in the suggestion that the hydrolysis and the alcoholysis of the latter involve oxyphosphorane intermediates.^{20,21}

Finally, the synthetic application of oxyphosphoranes is a promising field and should attract considerable interest in the future.^{1,8}

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