Nucleophilic Substitutions at Pentavalent Phosphorus. Reaction of 2,2,2-Trialkoxy-2,2-dihydro-1,3,2-dioxaphospholenes with Alcohols

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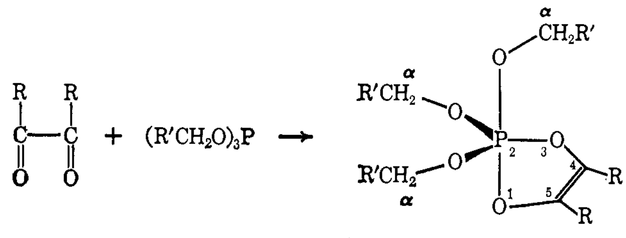
Abstract: Methanol was lost when 2,2,2-trimethoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene was treated with 1 molar equiv of benzyl alcohol at 100°. The products were the corresponding 2,2-dimethoxy-2-benzoxyphospholene (40%) and 2-methoxy-2,2-dibenzoxyphospholene (25%). In addition, 2,2,2-trimethoxyphospholene (30%) was recovered. Little or no phosphate esters were produced. The reaction of the 2,2,2-trimethoxyphospholene with 3 molar equiv of benzyl alcohol at 100° gave mostly the 2,2,2-tribenzoxyphospholene (60%) and some 2-methoxy-2,2-dibenzoxyphospholene (15%) but little phosphate esters. Tribenzoxyphospholene was also prepared from biacetyl and tribenzyl phosphite. The latter was made from tris(dimethylamino)phosphine and benzyl alcohol. P^{31} and H^1 nmr data are given.

The 2,2,2-trialkoxy-2,2-dihydro-1,3,2-dioxaphospholenes (I) can be prepared from the reaction of trialkyl phosphites with *o*-quinones, with *α*-diketones, and with other vicinal polycarbonyl compounds.[2]



I, $\delta P^{31} = ca. +45$ ppm *vs.* H_3PO_4

The X-ray analysis[3] of one of these phospholenes showed that the molecule in the crystal had the geometry of a trigonal bipyramid with the phosphorus at the center. The phospholene ring was in an apical equatorial position. The apical P–O bonds were longer than the corresponding equatorial P–O bonds. The apical P–O bond associated with the phospholene ring was longer than the apical P–O bonds leading to the alkoxy groups. Likewise, the equatorial P–O bond associated with the ring was longer than the equatorial P–O bonds leading to the alkoxy groups. There were four intramolecular nonbonded distances shorter than 3 Å, which must represent a severe internal over-crowding of the phospholene molecule. These distances were between an oxygen atom situated in a given position of the bipyramid and the *α*-carbon atom of the alkyl groups situated in other positions of the bipyramid. Acyclic pentaoxyphosphoranes have been prepared[4] from the reaction of trialkyl phosphites with dialkyl peroxides and appeared to be considerably less stable than the monocyclic oxyphosphoranes[2] and the spirooxyphosphoranes.[2a]

The P^{31} nmr shifts of the pentaoxyphosphoranes[2,5] were strongly positive relative to H_3PO_4. The H^1 nmr spectra of a number of phospholenes[2] derived from trimethyl phosphite showed only one doublet due to the three methoxy groups. The doublet was due to a coupling of the protons with the phosphorus. The magnetic equivalency of the three methoxy groups apparently resulted from a relatively rapid positional exchange among the groups in the trigonal bipyramid[2,6,7] at 20°. Several cases were examined also at −65° without significant changes.[2,8]

The investigation reported in this paper had two purposes: (1) to determine whether the alkoxy groups attached to the phosphorus in I could be replaced by other alkoxy groups upon reaction with alcohols without rupture of the five-membered ring; (2) to prepare a series of phospholenes of type I in which the *α*-carbons derived from the trialkyl phosphite portion had different steric requirements.

Results

2,2,2-Trimethoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene (II), prepared from the reaction of biacetyl with trimethyl phosphite,[2] was allowed to react with various molar ratios of benzyl alcohol at various temperatures. The methanol evolved in these reaction was collected, and the products of the reactions were analyzed by means of P^{31} and H^1 nmr spectrometry. The components of the mixtures were separated by

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(2) For recent reviews on these compounds, see: (a) F. Ramirez, M. Nagabhushanam, and C. P. Smith, *Tetrahedron*, in press; (b) F. Ramirez, H. J. Kugler, and C. P. Smith, *ibid.*, in press; (c) F. Ramirez, *Bull. Soc. Chim. France*, 2443 (1966); (d) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).

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

(4) (a) D. B. Denney and S. T. D. Gough, *ibid.*, **87**, 138 (1965); (b) D. B. Denney and L. Saferstein, *ibid.*, **88**, 1839 (1966).

(5) (a) F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, *Tetrahedron Letters*, 2151 (1966); (b) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, 30, 2575 (1965); (c) F. Ramirez, A. V. Patwardhan, N. Ramanathan, N. B. Desai, C. V. Greco, and S. R. Heller, *J. Amer. Chem. Soc.*, **87**, 543 (1965).

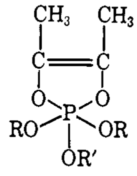
(6) F. Ramirez and N. B. Desai, *ibid.*, **85**, 3252 (1963).

(7) (a) S. R. Berry, *J. Chem. Phys.*, 32, 933 (1960); (b) E. L. Muetterties and R. A. Schumm, *Quart. Rev.* (London), 20, 245 (1966).

(8) The magnetic equivalency in the cyclic pentaoxyphosphorane at 20° and at −65° may not be a general phenomenon. The three methoxy groups of a related cyclic tetraoxyalkylphosphorane made from the reaction of 3-benzylidene-2,4-pentanedione with trimethyl phosphite (*cf.* F. Ramirez, O. P. Madan, and S. R. Heller, *J. Amer. Chem. Soc.*, **87**, 731 (1965)) were magnetically equivalent at 20° but not at −65° (*cf.* D. G. Gorenstein and F. H. Westheimer, *ibid.*, **89**, 2762 (1967); F. Ramirez, *Trans. N. Y. Acad. Sci.*, in press).

fractional distillation taking advantage of the relatively large differences in their boiling points. The H^1 nmr data are listed in Table I.

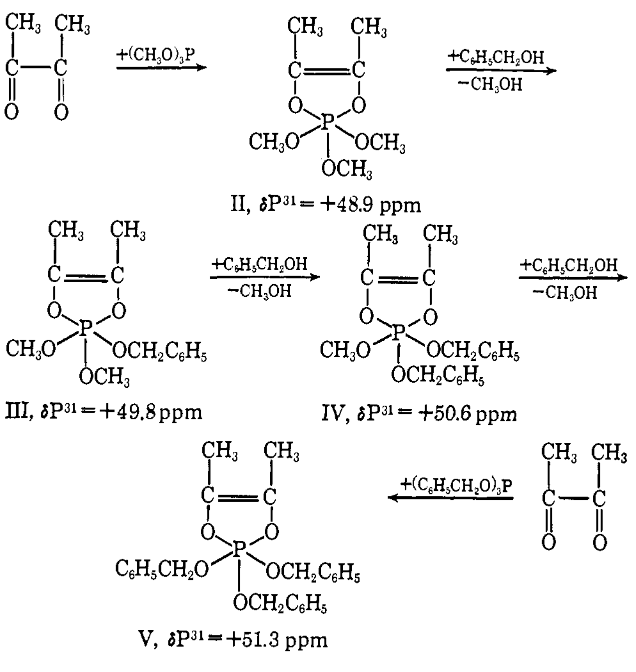
Table I. H^1 Nmr Data[a] for 2,2,2-Trialkoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholenes



R	R′	τ_{CH_3C}[b]	τ_{CH_3O}[c]	$J_{HP}^{CH_3O}$	τ_{CH_2O}[d]	$J_{HP}^{CH_2O}$
CH_3	CH_3	8.23	6.52	12.9	None	None
CH_3	$C_6H_5CH_2$	8.25	6.49	13.0	5.16	8.8
$C_6H_5CH_2$	CH_3	8.25	6.46	13.2	5.15	9.2
$C_6H_5CH_2$	$C_6H_5CH_2$	8.28	None	None	5.14	9.4

[a] Shifts in ppm from TMS = 10 (τ values); at 60 Mcps 20° in CCl_4 solution. Coupling constant, J, in cps. [b] One singlet; the two methyls were equivalent. [c] One doublet; the methoxy groups were equivalent. [d] One doublet; the benzoxy groups were equivalent.

Approximately 30% of the original trimethoxyphospholene II remained unchanged when treated with 1 molar equiv of benzyl alcohol at 100° for a period of 3 hr. II (40%) was converted into the dimethoxybenzoxyphospholene III, and 25% of II appeared as the methoxydibenzoxyphospholene IV under these conditions. No tribenzoxyphospholene V was detected. Less than 5% of phosphate esters were produced. The expected methanol (90%) was collected.



II, $\delta P^{31} = +48.9$ ppm

III, $\delta P^{31} = +49.8$ ppm

IV, $\delta P^{31} = +50.6$ ppm

V, $\delta P^{31} = +51.3$ ppm

The P^{31} nmr shifts are indicated under the corresponding formulas. The expected patterns of the P^{31} nmr spectra were constructed from the H^1–P^{31} coupling constants of Table I. They agreed well with the spectra determined at 40.5 Mcps as illustrated in Figure 1 for one of the phospholenes.

When the trimethoxyphospholene II was treated with 1.4 molar equiv of benzyl alcohol, the mixture of products consisted of unreacted phospholene II (13%), dimethoxybenzoxyphospholene III (38%), and methoxydibenzoxyphospholene IV (41%). The remaining material could not be characterized.

The reaction of the trimethoxyphospholene II with 3 molar equiv of benzyl alcohol at 100° gave at least 60% of the expected 2,2,2-tribenzoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene (V). About 15% of the methoxydibenzoxyphospholene IV was also formed. The unidentified by-products could contain some phosphate esters, but these were formed in relatively small amounts.

An authentic sample of the tribenzoxyphospholene V was prepared from biacetyl and tribenzyl phosphite.[9] The latter ester was conveniently prepared by the reaction of tris(dimethylamino)phosphine and benzyl alcohol following a procedure previously described[10] for the preparation of other phosphite esters.

$$[(CH_3)_2N]_3P + 3C_6H_5CH_2OH \longrightarrow (C_6H_5CH_2O)_3P + 3(CH_3)_2NH$$
$$\delta P^{31} = -138.6 \text{ ppm}$$

It was independently verified that the trimethoxyphospholene II in the absence of benzyl alcohol remained unchanged under the conditions of the alcoholyses; *i.e.*, the phospholene did not lose trimethyl phosphate nor dissociate into biacetyl and trimethyl phosphite when heated for 4 hr at 110° (165 mm).

Discussion

These experiments showed that the alkoxy groups attached to the phosphorus in certain 2,2,2-trialkoxy-2,2-dihydro-1,3,2-dioxaphospholenes (I) undergo successive replacements by other alkoxy groups upon reaction with alcohols. The extent of the substitution could be regulated by the relative amounts of the phospholene and of the alcohol. However, even when the reagents were used in equimolar amounts, disubstitution accompanied monosubstitution at the phosphorus atom. Trisubstitution was observed when 3 molar equiv of the alcohol was used.

The most striking result of this study was the absence of significant amounts of phosphate esters when the phospholene II was heated with benzyl alcohol at 100°. This should be compared with the tendency of acyclic pentaoxyphosphoranes to form phosphate esters.[4] A possible explanation of this difference is that the presence of a phospholene ring decreases significantly the intramolecular overcrowding which exists in the trigonal-bipyramidal structure[3] of the pentaoxyphosphoranes, and hence increases their stability.

The alcoholysis of the trimethoxyphospholene II was a relatively difficult process. For example, little reaction was observed when II was heated with 3 molar equiv of benzyl alcohol for 2 hr at 40° (165 mm). This reaction was nearly complete after 30 min at 110°. Note that the same phospholene II underwent a nearly instantaneous reaction with 1 molar equiv of water in benzene solution[11] at 0°. The products of this reaction

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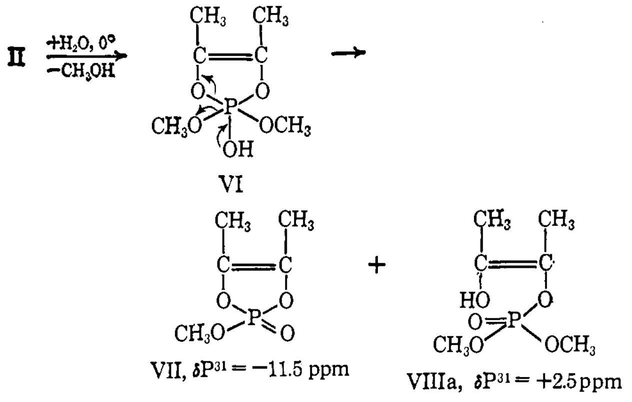
[9] (a) J. Baddiley, V. M. Clark, J. J. Michalski, and A. R. Todd, *J. Chem. Soc.*, 815 (1949); (b) W. Gerrard and B. D. Shepard, *ibid.*, 2069 (1953).

[10] (a) D. Houalla, N. Sanchez, and R. Wolf, *Bull. Soc. Chim. France*, 2368 (1965); (b) R. Burgada, *ibid.*, 347 (1967); (c) R. Burgada, *Ann. Chim.*, **8**, 347 (1963); (d) H. J. Vetter and H. Noth, *Ber.*, **96**, 1308 (1963).

[11] (a) F. Ramirez, O. P. Madan, and C. P. Smith, *J. Amer. Chem. Soc.*, **87**, 670 (1965); (b) D. Swank, C. N. Caughlan, F. Ramirez, O. P. Madan, and C. P. Smith, *ibid.*, **89**, 6503 (1967).

were acetoinenediol cyclophosphate (VII) and the enol form of dimethylphosphoacetoin (VIIIa). It was suggested that these products resulted from the decomposition of an intermediate cyclic hydroxytetraalkoxyphosphorane, VI.

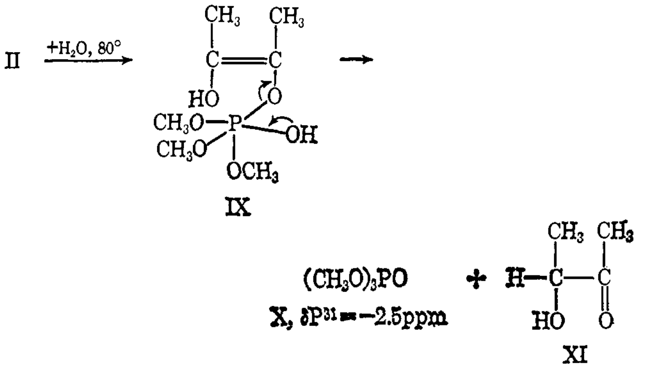


VI

VII, $\delta P^{31} = -11.5$ ppm

VIIIa, $\delta P^{31} = +2.5$ppm

When the hydrolysis of the phospholene II was carried out[11] at 80°, the products were mostly trimethyl phosphate (X) and acetoin (XI). It was suggested that at the higher temperature, the hydrolysis involved the open-chain hydroxytetraalkoxyphosphorane (IX), which tended to lose acetoin (XI) rather than methanol.[12]



IX

X, $\delta P^{31} = -2.5$ppm

XI

Several mechanisms are possible for the reactions of cyclic pentaoxyphosphoranes with alcohols:

(1) A concerted substitution at phosphorus *via* a transition state[13,14] which could have octahedral symmetry, for example, that shown in formula XII.

(2) A stepwise substitution involving an intermediate with a possible octahedral configuration, as for example in formula XIII.[14a] Compounds of this type with P–C and with P–O bonds have been reported recently,[15] and they have been known for some time in the case of the phosphorus halides.[16] Several geometries can be conceived for both the transition state XII and the intermediate XIII. The present data do not warrant further discussion of the stereochemical aspects of these substitutions.[17]

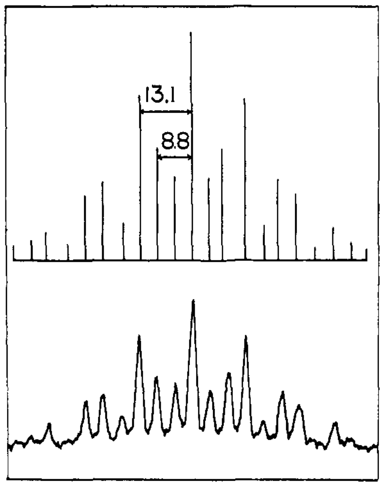
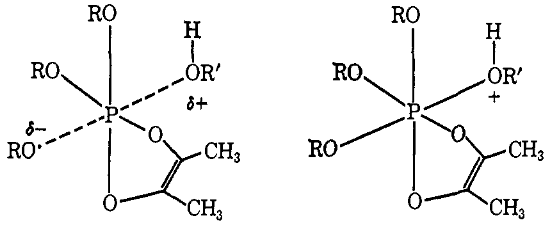


Figure 1. Calculated and observed P^{31} nmr spectrum of 2,2-dimethoxy-2-benzoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene. δP^{31} = +49.8 ppm *vs.* H_3PO_4. J_{CH_3OP} = 13.1 cps; $J_{C_6H_5CH_2OP}$ = 8.8 cps. In CCl_4 at 40.5 Mcps.



XII XIII

$R = CH_3$; $R' = C_6H_5CH_2$

(3) A preionization mechanism with retention of the five-membered ring. This assumes the intermediate formation of a cyclic ion pair XIV. The substitution by benzyl alcohol would follow this ionization.

(4) A preionization mechanism with rupture of the five-membered ring. In this case, the substitution would proceed *via* an open dipolar ion XV and could involve other intermediates like XVI and XVII.

We suggest that the results of the reaction of the biacetyl–trimethyl phosphite adduct II with benzyl alcohol are better explained by mechanisms 1 or 2 than by mechanisms 3 or 4. If a preionization with retention of the ring (formula XIV, mechanism 3) were involved in the substitution, one would expect the formation of some acetoinenediol cyclophosphate[11] VII. The latter could result simply by a nucleophilic attack by alkoxy

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[12] The hydrolyses of other types of five-membered cyclic pentaoxyphosphoranes to cyclic and open phosphate esters have also been described; see: (a) F. Ramirez, N. B. Desai and N. Ramanathan, *J. Am. Chem. Soc.*, **85**, 1874 (1963); (b) F. Ramirez, O. P. Madan, N. B. Desai, S. Meyerson, and E. M. Banas, *ibid.*, **85**, 2681 (1963); (c) F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963); (d) F. Ramirez, A. V. Patwardhan, N. B. Desai, and S. R. Heller, *ibid.*, **87**, 549 (1965); (e) F. Ramirez, S. B. Bhatia, and C. P. Smith, *ibid.*, **89**, 3026 (1967).

[13] For discussions of this problem in silicon chemistry, see: (a) L. A. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *ibid.*, **89**, 857 (1967); (b) L. A. Sommer, W. D. Korte, and T. G. Rodewald, *ibid.*, **89**, 862 (1967); and previous references.

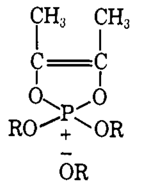
[14] Substitutions on the triphosphatriazene system have been discussed; see: (a) R. Keat, R. A. Shaw, and C. Stratton, *J. Chem. Soc.*, 2223 (1965); (b) C. Hills and R. A. Shaw, *ibid.*, 4059 (1965); (c) R. Keat and R. A. Shaw, *ibid.*, A908 (1966).

[14a] NOTE ADDED IN PROOF. R. G. Pearson and F. Basolo (*Inorg. Chem.*, **4**, 1524 (1965)) have suggested the formation of a 5-coordinated intermediate with trigonal-bipyramidal geometry in thebase hydrolysis of halogenoamminecobalt(IV) complexes. The addition of water to that intermediate, in the second step of the hydrolysis, is formally analogous to the addition of a nucleophile to the phosphorus of the oxyphosphorane.

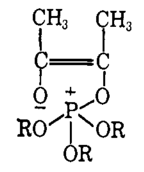
[15] (a) G. Wittig, *Bull. Soc. Chim. France*, 1162 (1966); (b) D. Hellwinkel, *Chem. Ber.*, **98**, 576 (1965); (c) G. Wittig and A. Maercker, *ibid.*, **97**, 747 (1964); (d) H. R. Allcock, *J. Amer. Chem. Soc.*, **86**, 2591 (1964).

[16] For recent reviews with many references, see: (a) R. Schmutzler, *Angew. Chem. Intern. Ed. Engl.*, **3**, 753 (1964); (b) *ibid.*, **4**, 496 (1965).

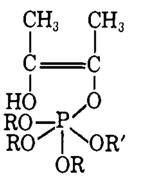
[17] For a comprehensive discussion of the stereochemistry of reactions of organosphorphorus compounds, see: W. E. McEwen, in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, pp 1–42.



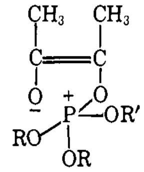
XIV, R = CH_3



XV, R = CH_3



XVI, R = CH_3; R′ = $C_6H_5CH_2$

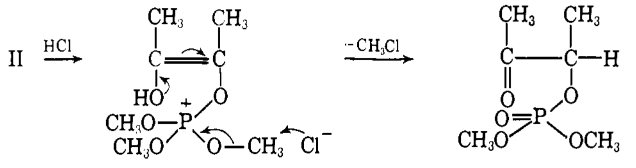


XVII, R = CH_3; R′ = $C_6H_5CH_2$

on the activated alkyl group of a tetraalkoxyphosphonium salt[18]

$$(RO)_3\overset{+}{P}\text{–O–R}\ \overset{-}{O}R' \longrightarrow (RO)_3P{=}O + ROR'$$

If a preionization with rupture of the ring (formulas XV–XVII, mechanism 4) were involved, one might expect the formation of some dimethylphosphoacetoin (VIIIa) or of a corresponding benzyl derivative; these together with the corresponding ethers, R_2O, ROR′, and R'_2O, would result from nucleophilic substitutions on the alkyl group of activated phosphonium salts as before. This type of behavior has already been observed[19] in the treatment of the phospholene II with hydrogen chloride, which gave dimethylphosphoacetoin (VIIIb) *via* the phosphonium salt XVIII.

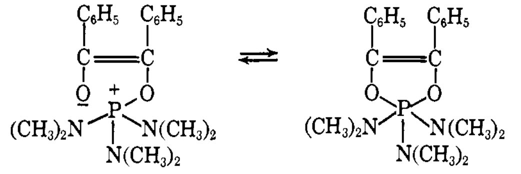


XVIII

VIIIb, $\delta P^{31} = +0.3$ppm

Note that the formation of an intermediate like XVI could lead also to the formation of acetoin (XI) and of phosphate esters like trimethyl phosphate, dimethylbenzyl phosphate, etc.; XVI + R′OH → XI + $(RO)_3P(OR')_2$ → $(RO)_3PO$ + R'_2O. This behavior would resemble the formation of trimethyl phosphate[11] and of acetoin (XI) in the hydrolysis of the phospholene II at 80°; IX → X + XI.

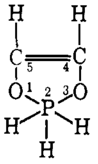
Although the results of the alcoholysis of the biacetyl–trimethyl phosphite adduct II are satisfactorily explained as a simple substitution of alkoxy groups on phosphorus (formulas XII and XIII, mechanism 1 or 2), it should be emphasized that there is direct evidence for the existence of open dipolar ions of type XV in certain related systems.[20] For example, the triaminooxyphosphonium dipolar ion XIX and the corresponding triaminodioxyphosphorane XX have been isolated in crystalline forms.[21] Solutions of these crystalline adducts contained the same molecular species in equilibrium with each other. Certain solvents favored the cyclic form with pentavalent phosphorus while others favored the dipolar ion with tetravalent phosphorus. The values of the P^{31} nmr shifts varied from +30.2 ppm in 0.8 *M* hexane to +13.1 ppm in 1.2 *M* CH_2Cl_2 solutions. Each value corresponds to an average of the negative value of the open structure XIX (*ca.* −35 ppm) and of the positive value of the cyclic form XX (*ca.* +37 ppm). Compounds of this type were extremely sensitive to both water and alcohols.



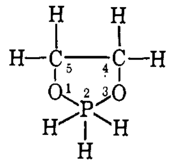
XIX

XX

The stability of derivatives of the 2,2-dihydro-1,3,2-dioxaphospholene and of the corresponding 2,2-dihydro-1,3,2-dioxaphospholane ring systems, XXI and XXII, respectively, depends on both electronic and steric characteristics of the substituents on the phosphorus atom; for example, the methoxy groups of II and the dimethylamino groups of XX. The nature of the substituents on positions 4 and 5 of these rings also affects their stability. The thermal behavior of these compounds and their behavior toward a variety of nucleophilic[22] and electrophilic[19,23] reagents will be determined to a great extent by these structural features.



XXI



XXII

Experimental Section

The analyses were performed by the Schwarzkopf Microanalytica Laboratory, Woodside, N.Y. All P^{31} nmr shifts are given in ppm from 85% H_3PO_4 as zero; they were determined at 40.5 Mcps. All H^1 nmr shifts are given in ppm from TMS = 10 (τ values); they were determined at 60 Mcps.

Reaction of 2,2,2-Trimethoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene with 1 Molar Equiv of Benzyl Alcohol. The biacetyl–trimethyl phosphite adduct II (26.17 g, 0.124 mol) and benzyl alcohol (13.61 g, 1 molar equiv) were mixed under N_2 at 20°. The mixture was kept 3 hr at 100° (*ca.* 200 mm). The liquid that distilled was identified as methanol (3.15 g, 0.1 mol). The residue of the distillation was analyzed by H^1 nmr spectrometry and was found to contain three major products: trimethoxy-, dimethoxybenzoxy-, and methoxydibenzoxy-4,5-dimethyl-2,2-dihydro-1,3,2-

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(18) (a) J. S. Cohen, *J. Amer. Chem. Soc.*, **89**, 2543 (1967); (b) J. D. Berlin, D. M. Hellwege, M. Nagabhushanam, and E. T. Goudy, *Tetrahedron*, 22, 2191 (1966); (c) D. B. Denney and J. Giacine, *Tetrahedron Letters*, 1747 (1964); (d) D. A. Schmideter, B. Wolf, and K. Düll, *Angew. Chem. Intern. Ed. Engl.*, 4, 712 (1965); (e) H. Teichmann, M. Jatkowski, and G. Hilgetag, *Angew. Chem. Intern. Ed. Engl.*, **6**, 372 (1967).

(19) F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, **82**, 2652 (1960).

(20) (a) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *ibid.*, **87**, 4973 (1965); (b) *ibid.*, **89**, 6276 (1967).

(21) (a) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron Letters*, 3053 (1966); (b) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron*, in press.

(22) The alcoholyses of derivatives of the phospholane ring system (XXII) can result in molecular rearrangement or in a simple elimination reaction depending on the structure of the phospholanes; see: (a) F. Ramirez and N. Ramanathan, *J. Org. Chem.* **26**, 3041 (1961); (b) F. Ramirez, S. B. Bhatia, and C. P. Smith, *Tetrahedron*, **23**, 2067 (1967); (c) F. Ramirez, S. B. Bhatia, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, 32, 2194 (1967); (d) F. Ramirez, S. B. Bhatia, A. V. Patwardhan, and C. P. Smith, *ibid.*, 32, 3547 (1967).

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dioxaphospholenes (II, III, and IV), in the amounts of 30, 40, and 25%, respectively.

The residue was distilled under vacuum. The liquid collected at 50–55° (0.5 mm) (10.78 g) was analyzed by H^1 and P^{31} nmr spectrometry and found to consist of the trimethoxyphospholene II (60%), dimethoxybenzoxyphospholene III (10%), trimethyl phosphate (20%), and benzyl alcohol (10%). The residue of this distillation (25.16 g) contained the dimethoxybenzoxyphospholene III (60%) and methoxydibenzoxyphospholene IV (40%).

The residue of the previous distillation (25.16 g) was submitted to fractional short-path distillation. (1) The *first fraction* (10.55 g, 30%) was collected at 95–97° (0.05 mm). Spectral analysis showed that this fraction consisted of at least 95% of the dimethoxybenzoxyphospholene III and of less than 5% of a phosphate ester. The latter was removed as a first fraction in a short-path redistillation. Pure **2,2-dimethoxy-2-benzoxy-4.5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene (III)** was collected at 96–97° (0.05 mm). The H^1 nmr signals are listed in Table I. The infrared spectrum in CCl_4 had bands at (μ): 3.44 (s), 5.76 (w), 6.69 (w), 6.90 (s), 6.99 (w), 7.21 (s), 7.29 (shoulder), 7.78 (s), 8.04 (s), 8.26 (w), 8.68 (s), 9.1–9.7 (broad and strong), 10.01 (s), and 10.28 (s).

Anal. Calcd for $C_{13}H_{19}O_5P$: C, 54.5; H, 6.7; P, 10.8. Found: C, 54.2; H, 6.4; P, 10.9.

(2) The *second fraction* (1.03 g, 14%) of the above distillation was collected at 96–100° (5×10^{-6} mm) and was **2-methoxy-2,2-dibenzoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene (IV).** The H^1 nmr signals are listed in Table I. The infrared spectrum in CCl_4 was very similar to the spectrum of the dimethoxybenzoxyphospholene III except that the relative intensities of some of the bands were different.

Anal. Calcd for $C_{19}H_{23}O_5P$: C, 63.0; H, 6.4; P, 8.5. Found: C, 62.9; H, 6.5; P, 8.5.

Reaction of the 2,2,2-Trimethoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene with 1.4 Molar Equiv of Benzyl Alcohol. The biacetyl–trimethyl phosphite adduct II and benzyl alcohol (1.4 molar equiv) were mixed under N_2. The mixture was heated 4 hr at 100° (*ca.* 50 mm). The distillate (6.03 g, 1.3 molar equiv) was shown to be methanol. The residue was analyzed and was fractionally distilled as indicated above. The trimethoxy-, dimethoxybenzoxy-, and methoxydibenzoxyphospholenes II, III, and IV were formed in 13, 38, and 41% yields, respectively. There was spectral evidence for the formation of 5% of tribenzyl phosphite, $(C_6H_5CH_2O)_3P$, which could have been formed in the reaction or during the fractional distillation.

Reaction of the 2,2,2-Trimethoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene with 3.4 Molar Equiv of Benzyl Alcohol. The biacetyl–trimethyl phosphite adduct II (5.80 g) was mixed with benzyl alcohol (10.14 g, 3.4 molar equiv) at 100° under N_2. The mixture was kept 12 hr at 100°, while a slow stream of N_2 was being bubbled through the solution. The gas stream was passed through a trap at −70° to collect the methanol. The residue was analyzed by H^1 and P^{31} nmr spectrometry and was found to consist of methoxydibenzoxyphospholene IV (15%), tribenzoxyphospholene V (60%), and small amounts of a phosphate ester. The identification of these products was based on the signals listed in Table I.

Other Alcoholyses of the Biacetyl–Trimethyl Phosphite Adduct II. (a) Equimolar amounts of the adduct II and benzyl alcohol were heated at 100° (170 mm). Practically all of the methanol evolved in this reaction was collected within 30 min. The residue was analyzed by H^1 and P^{31} nmr spectrometry to confirm the results described in the previous experiment carried out over a 3-hr period.

(b) The adduct II was kept with 3 molar equiv of benzyl alcohol for 2 hr at 40° (165 mm). No methanol was produced under these conditions. The expected amount of methanol was collected when the reaction mixture was heated for 30 min at 100° (165 mm).

Thermal Stability of the Biacetyl–Trimethyl Phosphite Adduct II. The adduct II was heated for 3.5 hr at 110° (165 mm). No volatile materials were collected in a trap fitted to the system and cooled at −70°. The residue was shown to be unreacted adduct II by H^1 nmr spectrometry.

Preparation of Tribenzyl Phosphite from the Reaction of Tris(dimethylamino)phosphine with Benzyl Alcohol. Tris(dimethylamino)phosphine (4.63 g) was mixed with benzyl alcohol (9.86 g, 3.2 molar equiv) at 20°. The mixture was kept 5 hr at *ca.* 100° while a show stream of N_2 was being bubbled through the solution. The gas stream was passed through a trap at −70° giving the dimethylamine. The residue (9.6 g, 96%) consisted of tribenzyl phosphite of 90% purity by H^1 nmr spectrometry. Short-path distillation gave tribenzyl phosphite, bp 142–148° (0.02 mm), in 60% yield; $\delta P^{31} = -138.6$ ppm (septet). The H^1 nmr spectrum in CCl_4 had a 15 H^1 signal at τ 2.8 and a 6 H^1 doublet at τ 5.26, $J_{HP} = 7.9$ cps. The infrared spectrum in CCl_4 had bands at (μ): 3.38, 3.49, 3.56, 6.25, 6.72, 6.92, 7.33, 8.00, 8.30, 8.40, 9.6–10.4 (broad and very strong), and 10.95.

Anal. Calcd for $C_{21}H_{21}O_3P$: C, 71.5; H, 6.0; P, 8.8. Found: C, 71.2; H, 6.3; P, 9.1.

Preparation of the Biacetyl–Tribenzyl Phosphite Adduct V. A solution of biacetyl (0.50 g) in anhydrous benzene (5 ml) was added dropwise to a solution of tribenzyl phosphite (2.11 g, 1.03 molar equiv) in benzene (3 ml) at 0° with stirring under N_2. The solution was kept 10 hr at 25° and was evaporated at 25°, first at 15 mm and then at 0.05 mm. The residue (2.54 g) was a colorless, thick oil that could not be distilled or crystallized. The spectral analysis disclosed that this residue consisted of 2,2,2-tribenzoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene (V) of at least 98% purity. The H^1 nmr signals are listed in Table I. The infrared spectrum in CCl_4 had bands at (μ): 3.37 (s), 3.48 (s), 5.78 (w), 6.70 (w), 6.90 (s), 7.00 (w), 7.22 (s), 7.30 (shoulder), 7.80 (s), 8.05 (s), 8.28 (s), 8.70 (s), 9.1–9.8 (broad and strong), and 10.3 (s). The crude material was submitted for analysis.

Anal. Calcd for $C_{25}H_{27}O_5P$: C, 68.5; H, 6.2; P, 7.0. Found: C, 67.5; H, 6.3; P, 6.5.

Celesticetin. V. The Structure of Celesticetin

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Abstract: The structure of celesticetin is β-salicyloyloxyethyl 6,8-dideoxy-6-(1-methyl-L-pyrrolidine-2-carboxamido)-7-O-methyl-1-α-thio-D-*erythro*-D-*galacto*-octopyranoside.

A partial structure[1] of celesticetin[2] (1) was incomplete as to questions regarding branching and stereoisomerism of the aminooctose as well as the relative locations of the methoxyl and amino groups on this sugar. Recent studies[3] on lincomycin (2) produced by

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