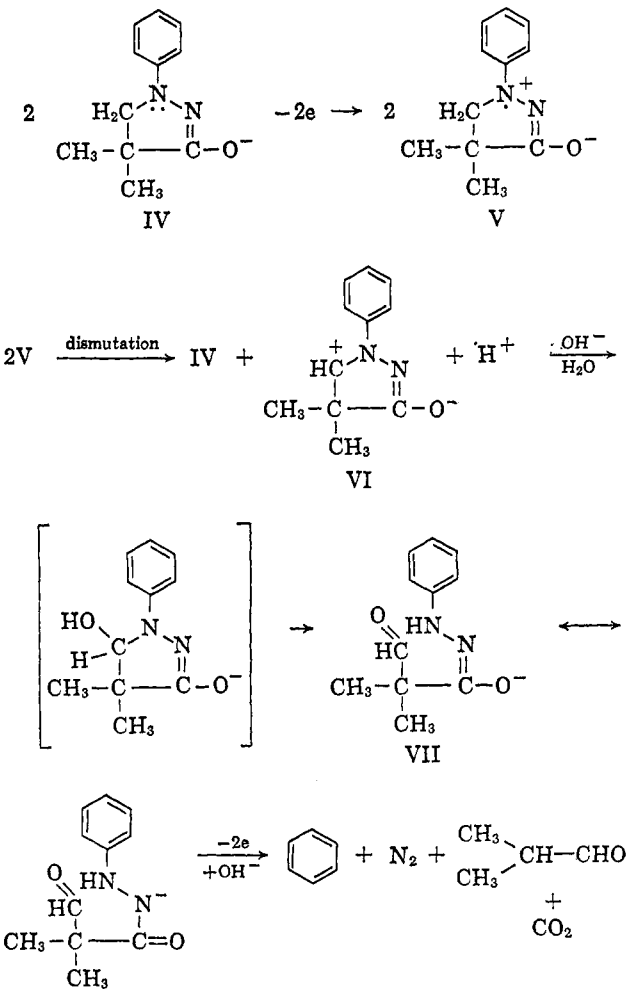
SCHEME I



whereas in 0.1 *N* sodium hydroxide solution, more than 5 equiv. of oxidant were required.) However, the addition of excess oxidant leads to the formation of a more resinous, polymeric material. Because of the formation of this very complex material, it was impossible to determine a mass balance for this reaction.

The steps in the oxidation reaction which follow the semiquinone dismutation are still uncertain. However, the following sequence, which is consistent with the observed stoichiometry of the reaction, accounts for the major products formed and is in agreement with the spectrochemical data. The reaction (Scheme I) can be visualized as proceeding by the loss of a single electron from the dissociated form of the pyrazolidinone IV to yield the semiquinone V. The dismutation of the semiquinone gives one molecule of IV and the electron-deficient intermediate VI, which can react with hydroxide ion to give a phenylhydrazide (VII). The major products of the reaction presumably arise by further oxidation of the hydrazide VII to the azo compound, followed by attack of hydroxide ion at the carbonyl carbon to yield benzene, nitrogen, isobutyraldehyde, and CO_2. The mode by which the minor products are formed remains obscure. However, the appearance of biphenyl, although in trace amounts, and the formation of high molecular weight polymeric materials, possibly by phenylation reactions, suggest that phenyl radicals may be formed at a relatively high concentration.

Acknowledgment.—The author should like to thank Dr. William C. Needler for his help and cooperation in providing the e.s.r. measurements and is grateful to Miss Thelma J. Davis, Mr. David P. Maier, and Dr. O. E. Schupp for infrared spectra, mass spectra, and gas chromatographic data, respectively.

Pentaoxyphosphoranes from the Reaction of Trialkyl Phosphites with α-Ketoaldehydes and with Vicinal Triketones. Condensations of α-Ketoaldehydes with α-Diketones. P^{31} and H^1 Nuclear Magnetic Resonance Spectra[1]

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Trialkyl phosphites reacted with diphenylpropanetrione and with phenylglyoxal yielding *1:1 adducts* formulated as cyclic unsaturated pentaoxyphosphoranes on the basis of P^{31} and H^1 n.m.r. spectra and infrared and ultraviolet spectra. The trione–phosphite adduct did not react with more trione. The ketoaldehyde–phosphite 1:1 adduct reacted with a second molecule of ketoaldehyde forming a *2:1 adduct* or cyclic saturated pentaoxyphosphorane, with a new carbon–carbon bond. In this condensation, two diastereoisomers (66:34) of one type of structure were obtained. The phenylglyoxal–phosphite 1:1 adduct condensed very slowly with biacetyl to give two diastereoisomers of a pentaoxyphosphorane; the latter were obtained, very rapidly, from condensation of the biacetyl–phosphite 1:1 adduct with phenylglyoxal.

Previous papers have described the preparation of cyclic unsaturated,[3] I and II, and cyclic saturated,[1d,3] III–VIII, pentaoxyphosphoranes[4] from condensation reactions of trialkyl phosphites with α-diketones, quinones, α-keto esters, and monofunctional aldehydes.

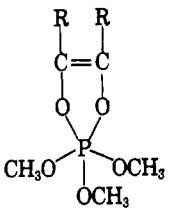
The pentacovalent character of the phosphorus in these derivatives of the 1,3,2-dioxaphospholene and dioxaphospholane ring systems was deduced from the relatively large positive shifts of the P^{31} n.m.r. signals relative to 85% phosphoric acid, from the positions of

(1) (a) Organic Compounds with Pentavalent Phosphorus. Part XXI; (b) Part XX: F. Ramirez, O. P. Madan, and C. P. Smith, *J. Am. Chem. Soc.*, **87**, 670 (1965); (c) Part XIX: F. Ramirez, H. J. Kugler, and C. P. Smith, *Tetrahedron Letters*, **No. 4**, 261 (1965); (d) Part XVIII: F. Ramirez, O. P. Madan, and S. R. Heller, *J. Am. Chem. Soc.*, **87**, 731 (1965).

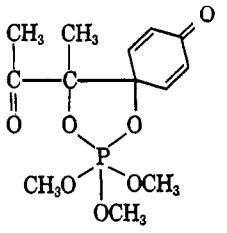
(2) This investigation was supported by Public Health Service Research Grant No. CA-04769-05 from the National Cancer Institute, and by National Science Foundation Grant G 19509.

(3) The literature has been reviewed by (a) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); (b) F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. B. Desai, *J. Am. Chem. Soc.*, **86**, 4394 (1964).

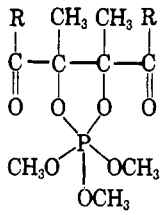
(4) For other pentaoxyphosphoranes, see (a) D. B. Denney and H. M. Reller, *ibid.*, **86**, 3897 (1964); (b) D. B. Denney and S. T. D. Gough, *ibid.*, **87**, 138 (1965).



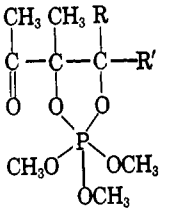
I, R = C_6H_5
II, R = CH_3



III

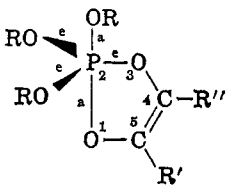


IV, R = CH_3
V, R = OCH_3



VI, R = CH_3; R′ = $COOCH_3$
VII, R = H; R′ = alkyl
VIII, R = H; R′ = C_6H_5

the H^1 n.m.r. signals of the methoxy groups attached to phosphorus and of the methyls and hydrogens attached to the phospholene and phospholane rings, and from the infrared and Raman spectra.[3] It is now known[5] from X-ray data that the phosphorus in the stable form of one of these oxyphosphoranes, the 9,10-phenanthraquinone–triisopropyl phosphite 1:1 adduct, is at the center of a nearly perfect trigonal bipyramid, IX, *i.e.*, the hybridization of the phosphorus seems to be sp^3d. The dioxaphospholene ring was situated in an apical–equatorial plane of the bipyramid, with the phenanthrene attached to an apical oxygen (1), and an equatorial oxygen (3), IX.



IX
1,3,2-dioxaphospholene
a = apical; e = equatorial

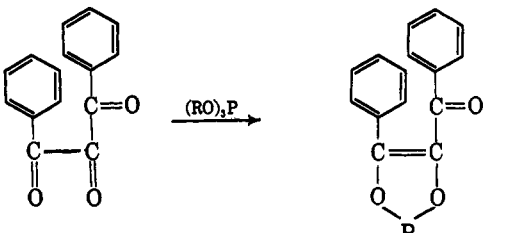
This paper describes the reactions of trialkyl phosphites with a vicinal triketone, diphenylpropanetrione (X), and an α-ketoaldehyde, phenylglyoxal (XIII).

Results

Preparation of 1:1 Adducts.—Diphenylpropanetrione (X) reacted with trimethyl phosphite (TMP) at 0° in anhydrous methylene chloride and formed a pale yellow noncrystalline 1:1 adduct in nearly quantitative yield. For reasons discussed in the next section this 1:1 adduct is formulated as a *cyclic unsaturated pentaoxyphosphorane*, XI. The 1:1 adduct could be distilled unchanged, but was sensitive to moisture. It was quite soluble in pentane.

The 1:1 adduct XII derived from the triketone and triisopropyl phosphite was obtained as yellow prisms, m.p. 46–48°.

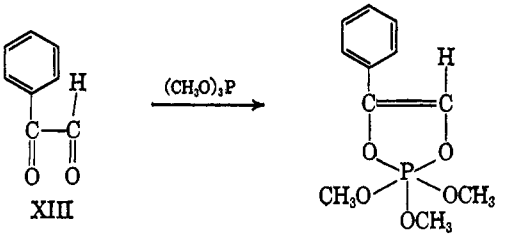
(5) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965).



X

XI, R = CH_3
XII, R = *i*-C_3H_7

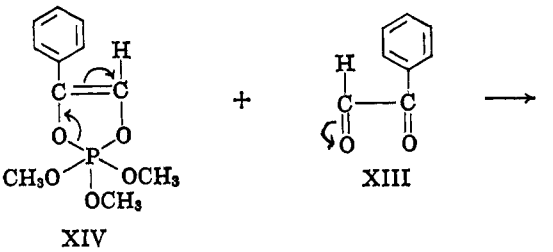
When a methylene chloride solution of phenylglyoxal XIII was slowly added to a large excess of TMP at 0°, a rapid reaction occurred. Under these conditions, a colorless, liquid 1:1 adduct could be isolated in about 50% yield. The evidence summarized below shows that this adduct has the unsaturated pentaoxyphosphorane structure, XIV.



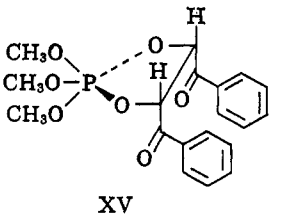
XIII

XIV

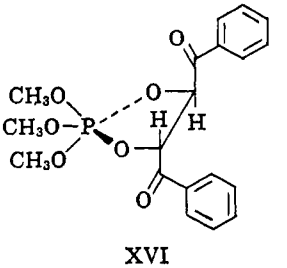
Preparation of 2:1 Adducts.—Even in the presence of a large excess of phosphite, the phenylglyoxal–TMP 1:1 adduct, XIV, was always accompanied by a second adduct in which two molecules of ketoaldehyde had been combined with one molecule of phosphite. This 2:1 adduct was prepared in nearly quantitative yield from the rapid reaction of 1:1 adduct, XIV, with phenylglyoxal (XIII). Two diastereoisomers were formed: the major isomer (*ca.* 65%) is assigned the structure of *meso*-2,2,2-trimethoxy-4,5-dibenzoyl-1,3,2-dioxaphospholane (XV) and the minor isomer (*ca.* 35%) that of the racemic form, XVI.



XIV XIII



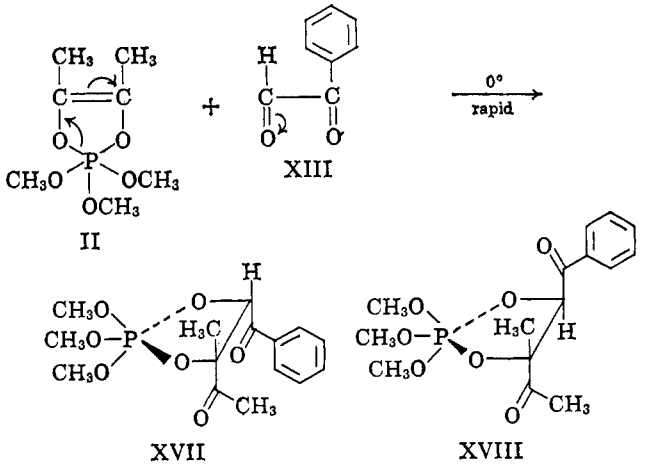
XV



XVI

The behavior of the previously reported[3,6] biacetyl–TMP 1:1 adduct, II, with phenylglyoxal (XIII) was then investigated. A rapid reaction occurred when 1 mole of the aldehyde XIII was added to 1 mole

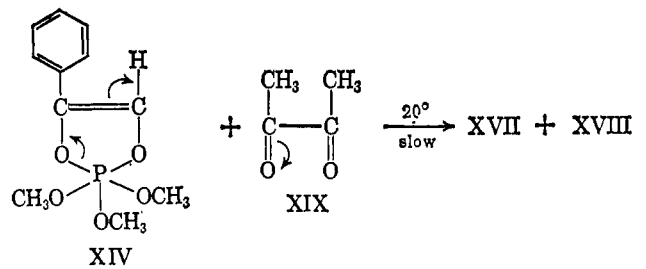
of the biacetyl–TMP adduct, II, in methylene chloride at 0°. The condensation was quantitative and the product contained only aliphatic and aromatic ketone carbonyls and no aldehyde carbonyls in the infrared spectrum. This product was a distillable, colorless oil which contained two diastereomers of an oxyphosphorane: 2,2,2-trimethoxy-4β-methyl-4-α-acetyl-5α-benzoyl-1,3,2-dioxaphospholane (XVII) and 2,2,2-trimethoxy-4β-methyl-4α-acetyl-5β-benzoyl-1,3,2-dioxaphospholane (XVIII). The configuration with *cis* acetyl/benzoyl, XVII, is assigned to the major isomer (85%) for reasons given below. The proportion of isomers (XVII:XVIII, 85:15) did not change when the solvent was omitted.



II XIII XVII XVIII

The biacetyl–phenylglyoxal–TMP adducts, XVII and XVIII, were relatively stable; however, the H^1 n.m.r. of methylene chloride solutions began to show the formation of some trimethyl phosphate after 7 days at 20°. There was no indication of a change in the ratio of isomers XVII and XVIII on standing in the solvent.

The reaction of the phenylglyoxal–TMP adduct, XIV, with biacetyl (XIX) was impractically slow in methylene chloride solution at 20°. A great deal of unconverted reagents was observable even after 13 days. When 1 mole of the adduct, XIV, and 3 moles of biacetyl (XIX) were kept 10 days at 20°, in the absence of additional solvent, a nearly complete disappearance of the 1:1 adduct occurred. The product had the same structure, XVII + XVIII, as the product from the reaction of the biacetyl–TMP adduct, II, with phenylglyoxal (XIII). However, the isomer ratio in both reactions was significantly different: 85% XVII and 15% XVIII from the adduct–aldehyde



XIV XIX

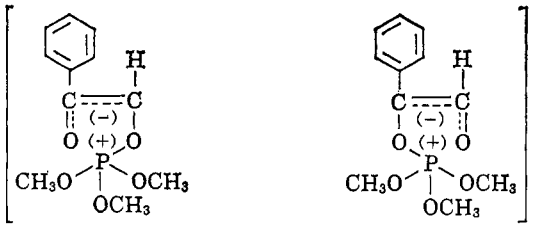
(6) (a) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **82**, 2652 (1960); (b) *ibid.*, **85**, 3252 (1963); (c) G. H. Birum and J. L. Dever, Abstracts, 135th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1958, p. 101P; (d) V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **121**, 466 (1958); (e) V. A. Kukhtin and K. M. Orekhova, *J. Gen. Chem. USSR*, **30**, 1229 (1960); (f) V. A. Kukhtin and K. M. Kirillova, *ibid.*, **32**, 2755 (1962).

reaction, II + XIII; 60% XVII and 40% XVIII from the adduct–diketone reaction, XIV + XIX. These figures were derived from the integrated intensities of the H^1 n.m.r. signals, as described in the Experimental section.

The condensation between an aliphatic α-diketone and an aromatic α-ketoaldehyde can be achieved rapidly and in excellent yields using trialkyl phosphites, by the simple expedient of forming first the α-diketone–phosphite 1:1 adduct and treating this with the aromatic α-ketoaldehyde. The alternate combination does not appear to be practical, but should be tested in each case involved, in particular, if different ratios of geometrical isomers are desirable.

Structure of the 1:1 Adducts Based on Physical Data. A.—The H^1 n.m.r. spectrum of the triketone–trimethyl phosphite adduct, XI, had *one* 9H doublet, J_{HP} = 13.2 c.p.s., at 6.42 p.p.m. in the τ scale, due to the three methoxy groups which are equivalent under the conditions of the measurements.[3,7] The aromatic protons gave multiplets at τ 2.1 ($4H^1$) and 2.7 ($6H^1$). The spectrum of the isopropyl phosphite–adduct, XII, is given in the Experimental section.

The three methoxy groups of the phenylglyoxal–TMP 1:1 adduct, XIV, appeared again as one doublet, J_{HP} = 13 c.p.s., at τ 6.40. The ring proton gave one doublet, J_{HP} = 32 c.p.s., at τ 2.97; *i.e., this proton has vinyl character* and shows a *relatively large coupling with the* P^{31} *nucleus.*[3,7,8] These features favor the cyclic structure XIV over the open dipolar structures, XIVa or XIVb.



XIVa XIVb

B.—The P^{31} n.m.r. spectrum[3,7] of the triketone–TMP adduct, XI, is reproduced in Figure 1. It agrees with the theoretical spectrum, which should have 10 lines, since the phosphorus nucleus is coupled with nine methoxy protons. *The signal due to the phosphorus is at considerably higher magnetic field in the triketone adduct, than in 85% phosphoric acid,* which is used as primary reference; *i.e.*, the phosphorus nucleus is more effectively shielded by electrons in the adduct than in phosphoric acid. The chemical shift is given in Table I. Table I includes also new values for other *o*-quinone–tertiary phosphite and α-diketone–tertiary phosphite 1:1 adducts[3,6,7] obtained under comparable conditions.

The P^{31} n.m.r. spectrum of the triketone–triisopropyl phosphite adduct, XII, should have four lines since the phosphorus nucleus is coupled with three protons. The four lines were clearly visible at 40.5 Mc./sec;

(7) References to pertinent work on chemical shifts and coupling constants in the H^1 and P^{31} n.m.r. spectra and calibration procedures will be found in (a) F. Ramirez, A. V. Patwardhan, N. Ramanathan, N. B. Desai, C. V. Greco, and S. R. Heller, *J. Am. Chem. Soc.*, **87**, 543 (1965); (b) F. Ramirez, A. V. Patwardhan, N. B. Desai, and S. R. Heller, *ibid.*, **87**, 549 (1965).

(8) (a) J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962); (b) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 87.

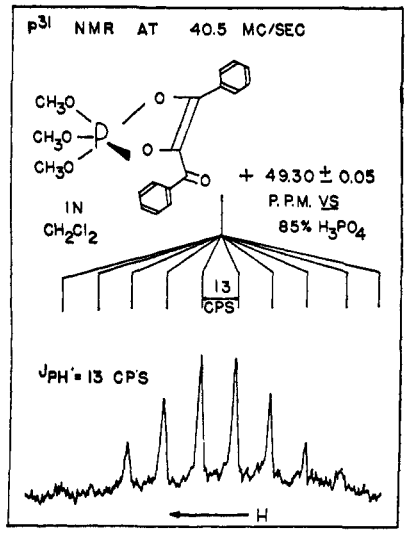
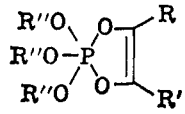
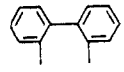
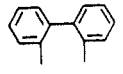
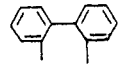


Figure 1.

TABLE I

CHEMICAL SHIFTS IN THE P^{31} N.M.R. SPECTRA OF CYCLIC UNSATURATED PENTAOXYPHOSPHORANES



R	R′	R″	δP^{31}[a,b]
C_6H_5	$-C(=O)-C_6H_5$	CH_3	+49.30[c]
C_6H_5	C_6H_5	CH_3	+49.50[c,d]
CH_3	CH_3	CH_3	+48.92[d,e]
C_6H_5	H	CH_3	+45.41[f]
			
		CH_3	+44.68[c,d]
C_6H_5	$-C(=O)-C_6H_5$	i-C_3H_7	+54.90[c]
C_6H_5	C_6H_5	i-C_3H_7	+53.86[c,d]
CH_3	CH_3	i-C_3H_7	+53.20[d,e]
			
		i-C_3H_7	+48.90[c,d]
C_6H_5	C_6H_5	C_6H_5	+62.50[c,d]
		C_6H_5	+58.66[c,d]
			

[a] Chemical shifts in p.p.m. ± 0.05 *vs.* 85% H_3PO_4 at 40.5 Mc./sec. in a Varian HR-100 spectrometer. [b] $(CH_3O)_3P$, −140.00 p.p.m.; $(CH_3O)_3PO$, −2.5 p.p.m. [c] Solvent CH_2Cl_2. [d] See ref. 3. [e] Pure liquid. [f] Solvent CCl_4.

the coupling constant was about 8 c.p.s. The strongly positive chemical shift is given in Table I and should be compared with other isopropyl phosphite adducts.

The P^{31} spectrum of the phenylglyoxal–trimethyl phosphite 1:1 adduct, XIV, is shown in Figure 2, and agrees with the theoretical spectrum. The phosphorus signal is split into a doublet by the ring proton;

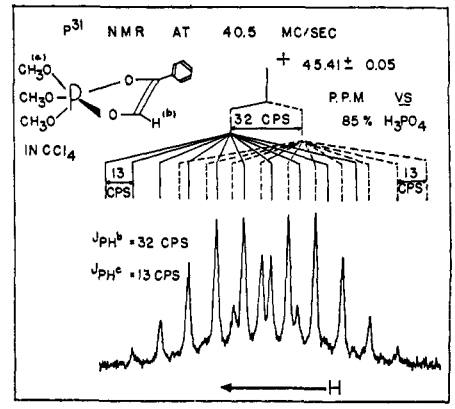
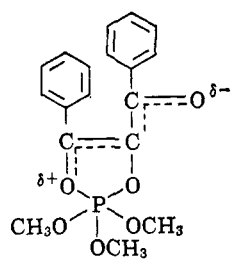


Figure 2.

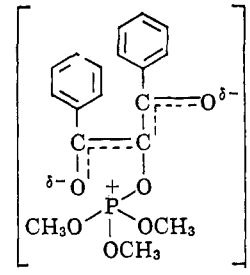
each of these is split into a decet by the nine methoxy protons. The chemical shift is positive (*cf.* Table I.)

C.—The infrared spectrum of the triketone–TMP adduct, XI, is reproduced in Figure 3 because it discloses an unusual feature of these cyclic unsaturated oxyphosphoranes: *the stretching vibration of the carbonyl function appeared at a rather long wave length, 6.45 μ (1550 cm.$^{-1}$).* The bands at 6.29 and 6.33 μ (1595 and 1580 cm.$^{-1}$) and at 6.71 μ (1490 cm.$^{-1}$) are attributed[9] to the C=C stretching vibrations of the aromatic rings conjugated with C=O and C=C functions. The band at 6.08 μ (1645 cm.$^{-1}$) is assigned[9] to the olefinic C=C. The olefinic C=C band in the phenylglyoxal adduct, XIV, was at 6.06 μ (1650 cm.$^{-1}$); the corresponding band in the benzil–phosphite adduct,[3] I, was at 6.02 μ (1665 cm.$^{-1}$).

To account for the position of the C=O stretching vibration in adduct XI (Figure 3) we suggest that structure XIa, in which the phosphorus retains the pentacovalent character, contributes significantly to the ground state of the oxyphosphorane. An open dipolar structure, XIb, would be inconsistent with other physical properties, for example, the P^{31} n.m.r. spectrum.



XIa



XIb, not formed

The strongest bands in the infrared spectra of the oxyphosphoranes XI and XIV were at 9.2 and 9.4 μ and are due to the P–O–CH_3 groups.[3,9]

The yellow triketone adduct XII absorbed strongly in the ultraviolet, with λ_{max} at 346 mμ (ε 8000) and 250 mμ (ε 19,000).

Structure of the 2:1 Adducts.—Three *structural* isomers of a cyclic saturated pentaoxyphosphorane can be derived from the combination of two molecules of phenylglyoxal with one molecule of trimethyl phosphite. Each of these structures is capable of existing

(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

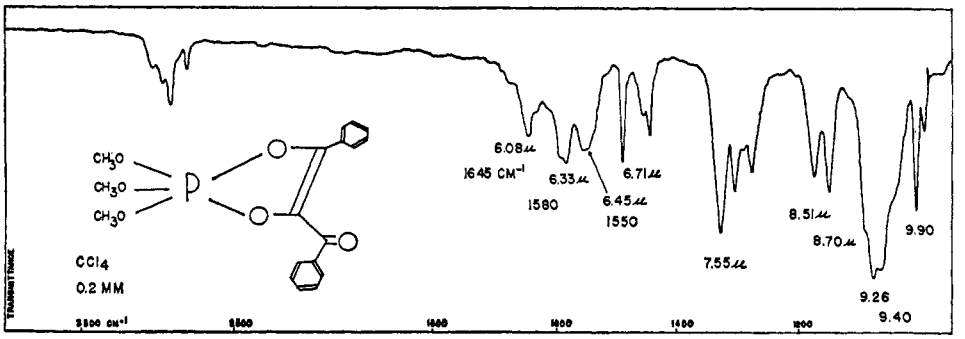


Figure 3.

in two diastereomeric forms. Formulas XV and XVI are based on the following evidence.

(1) The infrared spectrum of the mixture of isomers (XV + XVI) had one carbonyl band at 5.93 μ (1685 cm.$^{-1}$), which is typical of benzoyl functions,[9] and therefore excludes structural isomers with aldehyde functions. The pure crystalline isomer XV had a similar spectrum.

(2) The 2H^1 doublet, J_{HP} = 18 c.p.s., due to the ring protons of the *major isomer* was at a slightly lower magnetic field, τ 4.50, than the corresponding doublet, J_{HP} = 13 c.p.s., of the *minor isomer*, τ 4.55. The major isomer would have the *meso*-XV configuration (*cis* benzoyl/benzoyl), and the minor isomer the *racemic*-XVI configuration (*trans* benzoyl/benzoyl), on the assumption that a ring proton should be more shielded by a benzoyl group than by another ring proton. Although this assignment is not compelling, it leads to better correlations with other 2:1 adducts[3,7] (*vide infra*). The 9H^1 doublet, J_{HP} = 13 c.p.s., due to the three methoxy groups of the major isomer XV was at a somewhat higher field, τ 6.56, than the corresponding doublet, J_{HP} = 13 c.p.s., of the minor isomer, τ 6.46. The same relationship was observed[3] among the *meso*-IV and racemic-IV isomers of the biacetyl–TMP 2:1 adducts.

(3) The P^{31} n.m.r. spectrum of the crystalline major isomer, XV (Figure 4), had a multiplet centered at +46.9 p.p.m. *vs.* 85% H_3PO_4. This can be interpreted as a P^{31} signal split by the two ring protons into a triplet, J_{HP} = 18 c.p.s. (*cf.* H^1 n.m.r.), each member has been split by the nine methoxy protons into a decet, J_{PH} = 13 c.p.s. As shown in Figure 4, the detectable lines conform to this pattern of 30 lines.

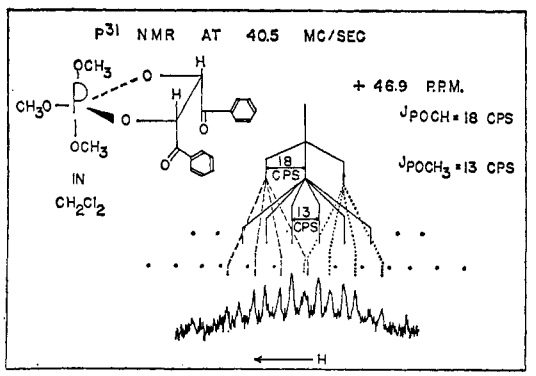


Figure 4.

Formulas XVII and XVIII for the biacetyl–phenylglyoxal–trimethylphosphite adducts follow from (4) the infrared spectrum, with an aliphatic ketone band at 5.74 μ and an aromatic ketone band at 5.92 μ plus the very strong $POCH_3$ bands at 9.16 and 9.40 μ; and (5) the doublet, J_{HP} = 18 c.p.s., due to the ring proton of the *major isomer* being at a significantly higher magnetic field, τ 4.95, than the corresponding doublet, J_{HP} = 23 c.p.s., of the minor isomer, τ 4.03. This is reasonable for configurations XVII, with *cis* acetyl/benzoyl, and XVIII, with *trans* acetyl/benzoyl, if it is assumed that a ring proton is more effectively shielded by an adjacent methyl group than by an adjacent acetyl group. In agreement with this assignment of configuration is the observation that the singlet due to the ring methyl of the major isomer, XVII, is at considerably lower field, τ 8.54, than the corresponding singlet of the minor isomer, XVIII, at τ 8.95. In the latter, the ring methyl is adjacent to a benzoyl group, while in the former, the ring methyl is adjacent to a ring proton.

There was no significant difference in the position of the acetyl protons, τ 7.75, in both isomers, XVII and XVIII, as shown by integration values. However, as before, the 9H^1 doublet, J_{HP} = 13 c.p.s., due to the methoxy groups of the major isomer, XVII, was at a somewhat higher field, τ 6.50, than the corresponding doublet, J_{HP} = 13 c.p.s., of the minor isomer, XVIII, at τ 6.42.

(6) The P^{31} n.m.r. spectrum of the mixture of stereoisomers, XVII and XVIII (85 and 15%, respectively), had 16 detectable lines centered at +50.08 ± 0.04 p.p.m. *vs.* 85% H_3PO_4. The multiplet corresponded to a P^{31} signal split into a doublet, J_{PH} = 18 c.p.s., by the ring proton; each component has been split into a decet, J_{PH} = 13 c.p.s. by the nine methoxy protons. There was some asymmetry in this multiplet toward lower field due to the minor isomer, XVIII.

Discussion

Relative Reactivities of 1,3,2-Dioxaphospholenes (Unsaturated Oxyphosphoranes) and of Polycarbonyl Acceptors.—The various combinations of unsaturated oxyphosphoranes and polycarbonyl acceptors investigated in this paper are listed in Table II in the order of decreasing reactivity.

The reactivity of the carbonyl acceptor is as expected for a nucleophilic addition to carbonyl carbon. The aldehyde function is more reactive than the ketone function. Both are activated by a vicinal keto group.

The relative reactivities of the 1:1 adducts suggest that a phenyl ring attached to the dioxaphospholene ring results in significant stabilization of this system, since the phenylglyoxal–TMP adduct was always

TABLE II
REACTIVITY OF DIOXAPHOSPHOLENES TO POLYCARBONYL COMPOUNDS[a]

1:1 adduct	Carbonyl acceptor
Biacetyl–TMP[b]	Phenylglyoxal
Phenylglyoxal–TMP	Phenylglyoxal
Biacetyl–TMP	Biacetyl
Phenylglyoxal–TMP	Biacetyl
1,3-Diphenylpropanetrione–TMP[c]	Phenylglyoxal
	Propanetrione

[a] Listed in order of decreasing reactivity. [b] TMP = trimethyl phosphite. [c] Does not react at 20° or at 100°.

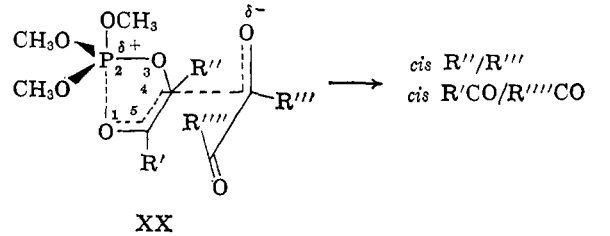
less reactive than the biacetyl–TMP adduct toward a given carbonyl acceptor. As expected from these results, the dioxaphospholene ring carrying both a phenyl ring and a benzoyl group was quite stable, presumably to owing conjugation of these groups with the ring C=C bond. So far, no acceptor capable of eliciting reactivity from the diphenylpropanetrione–TMP adduct has been found.

The interplay of effects in both the adducts and the carbonyl acceptor is shown by the greater reactivity of the phenylglyoxal–TMP adduct to phenylglyoxal than of the biacetyl–TMP adduct to biacetyl.

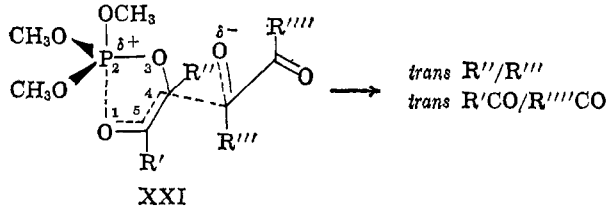
Mechanism and Stereochemistry.—A rupture of one of the two phosphorus–oxygen bonds of the dioxaphospholene ring, prior to reaction with the carbonyl acceptor, is probably not the slow step of the oxyphosphorane condensation. Two different open dipolar structures, XIVa and XIVb, would result from the rupture of the ring in the phenylglyoxal–TMP adduct, XIV. Structure XIVb has a negative charge partly delocalized on a benzylic carbon and should be more stable than XIVa. However, XIVb is not involved in the condensation, since the nucleophilic site of the molecule is, in fact, the carbon atom which carries the hydrogen, as in XIVa. Therefore, if XIVb is initially formed, it must revert to XIVa before it condenses with the carbonyl acceptor.

The condensation is probably a concerted process in which a P–O bond breaks as a C–C bond forms. This is suggested in transition states XX (leading to the *cis* isomer) and XXI (leading to the *trans* isomer). Perhaps very little or no separation of charge between phosphorus and oxygen actually occurs. The new dioxaphospholane ring could be formed as the dioxaphospholene ring is being broken.

Formulas XX and XXI are based on the X-ray analysis of the stable crystalline form of the 9,10-phenanthraquinone–triisopropyl phosphite 1:1 adduct,[5] mentioned in the introduction; *cf.* formula IX. The molecule is rather crowded. The apical ring oxygen (O-1 of the dioxaphospholene) is 1.76 Å. from the phosphorus and 2.69 Å. from its nearest neighbor (the carbon attached to the rear equatorial oxygen in XX or IX). The equatorial ring oxygen (O-3) is 1.60 Å. from the phosphorus and 2.80 Å. from its nearest neighbor (the carbon attached to the top apical oxygen in XX or IX). The dioxaphospholene ring is accessible from the face of the trigonal bipyramid defined by the two ring oxygens and the front equatorial oxygen. (The carbon on this front equatorial oxygen points upward and away from the phospholene ring; the C–O–P angle is 126°.)



XX



XXI

The nucleophilic carbon (C-4 in XX) is identified from the structure of the 2:1 adduct (R'' will be attached to the ring carbon). The reactive site of the acceptor carbonyl is also known from the structure of the product (R''' will be attached to the ring carbon). The oxygen of the acceptor carbonyl points upward, as shown in *both* XX and XXI, to minimize the separation between the phosphorus and the oxygen that must combine in the product. In this arrangement, the apical P–O (1) bond breaks in the transition state.[10,11]

The stereochemistry of the product will be determined by (1) the relative sizes of groups R'' and R''', *i.e.*, of the groups attached to the nucleophilic carbon of the phospholene and to the reactive carbonyl carbon of the acceptor; and (2) the attraction between the R'CO and the R''''CO groups. The oxygen atom of one can come close to the carbon atom of the other as the product is being formed.

The larger the groups R'' and R''', the greater the tendency toward *trans* R''/R''' isomer (XXI). The greater the attraction between R'CO and R''''CO, the greater the tendency toward *cis* R'CO/R''''CO (XX).

These generalizations account well for the proportions of stereoisomers observed[3,7] in the formation of the dioxaphospholanes IV–VIII and XV–XVIII.

In the fast condensation of the biacetyl–TMP 1:1 adduct (XX, R' = R'' = CH_3) with phenylglyoxal (XX, R''' = H; R'''' = C_6H_5), a great deal of *cis* isomer is formed (85:15, *cis–trans*) probably because the CH_3–H repulsion is small and the acetyl–benzoyl attraction is significant. The acceptor molecule with a small aldehyde (R'''CO) "fits" well in the orientation of XX. In the slow condensation of the phenylglyoxal–TMP 1:1 adduct (XX, R'' = H; R' = C_6H_5) with biacetyl (XX, R''' = R'''' = CH_3), less *cis* isomer is formed (60:40, *cis–trans*.) The differences in the proportions of the stereoisomers are not due to equilibration among them. The reactions were carried out under comparable conditions. The two sets of transition states XX and XXI apparently do not have

(10) The positions of groups R'' and R' on the phospholene ring can be reversed in XX. The orientation of the acceptor molecule is then reversed to place the reactive carbonyl, with group R''', next to the nucleophile C-5 on the apical oxygen (1). The same product is obtained by rupture of the equatorial P–O (3) bond in the transition state. Since the molecule seems to be more crowded around the C-4 than the C-5 bond, it is perhaps preferable to place the smallest group on C-4; *i.e.*, R'' < R', if they are not equal.

(11) In discussing possible geometries for the *transition states* in the acid hydrolysis of ethylene hydrogen phosphate, and in the exchange of oxygen between the latter and the water solvent, P. C. Haake and F. H. Westheimer [*J. Am. Chem. Soc.*, **83**, 1102 (1961)] have suggested structures in which the five-membered ring is in an apical–equatorial position, as has been found to be the case in the *stable form* of one of the cyclic pentaoxyphosphoranes.[5]

identical relative energies in both condensations. The extent of bond making *vs.* bond breaking in the transition states, the differences in reactivities and in sizes between an aldehyde *vs.* a methyl ketone and between a benzoyl *vs.* an acetyl (phenylglyoxal *vs.* biacetyl), and the differences in stabilities, and hence in reactivities of the dioxaphospholenes, could account for the isomer ratios and for the relative rates in the two condensations.

P^{31} N.m.r. Spectra of Cyclic Pentaoxyphosphoranes.[3,7]—A few correlations between structure and P^{31} chemical shift can be deduced from Table I. (1) The structure of the phosphite affects the chemical shift significantly: the shift is more positive in the phenyl phosphite adducts. (2) The chemical shift is not greatly affected by some types of substitutions at the olefinic carbons of the five-membered ring: two methyls, two phenyls, and a phenyl and a benzoyl group contribute about the same to the value of the shift. (3) Replacement of one phenyl group on the ring by a hydrogen atom results in a decrease in the positive value of the chemical shift. (4) When the two phenyl groups are connected by a bond, as in the adducts from phenanthraquinone, the chemical shift becomes less positive and is similar to the shift of a compound having only one phenyl ring in conjugation with the olefinic bond.

Among the cyclic oxyphosphoranes, the coupling constants[3,7,8] for the ring proton and the phosphorus decrease in the order: XIV (32 c.p.s.) > *trans*-XVIII (23 c.p.s.) > *cis*-XVII = *cis*-XV (18 c.p.s.) > *trans*-XVI (13 c.p.s.) > VIII (5.6 c.p.s.; *cis* acetyl/phenyl). In the phenylglyoxal–TMP 1:1 adduct, XIV, the dihedral angle[7,8] between the planes P–O–C and H–C–O in the ring POCH system is 180°. It seems reasonable to assume that the decrease in the proton–phosphorus coupling reflects a decrease in this dihedral angle towards 90°, as a result of changes in the shape of the dioxaphospholane ring.[7,8,12] The shape of the ring[8,12] should vary with the configuration and with the size and the dipole moment of the groups attached to the ring. A threefold variation (from 14 to 4.4 c.p.s.) in the coupling constant for the ring proton and the phosphorus has been observed[7b] in the two diastereomers *at phosphorus* of the cyclic phosphate ester obtained by hydrolysis of the biacetyl–propionaldehyde–TMP adduct VII. (In VII, R′ = ethyl *cis* to the acetyl in both diastereomers *at phosphorus*, one with the phosphoryl oxygen *trans* to the acetyl, the other with that oxygen *cis* to the acetyl.)

Experimental

The P^{31} n.m.r. spectra were determined at 40.5 Mc./sec. in a Varian HR-100 instrument. For calibration see ref. 7.

The H^1 n.m.r. spectra were determined at 60 Mc/sec. in a Varian A-60 instrument by standard techniques using tetramethylsilane as internal reference. The infrared spectra were determined in a Perkin-Elmer Model 21 instrument.

Reaction of Trimethyl Phosphite with Diphenylpropanetrione (X).—A solution of diphenylpropanetrione (15.8 g.) in anhydrous methylene chloride (20 ml.) was added dropwise to a solution of trimethyl phosphite (9.1 g., 1.1 mole equiv.; dried over Na wire and distilled) in 5 ml. of methylene chloride at 0–5° over a 1-hr. period with stirring under N_2. The solution became pale yellow and considerable heat was evolved. The solution was kept 64 hr. at 20° without appreciable change in the infrared spectrum. The solvent was removed at 20° (15 mm.), and the excess of phosphite at 50° (2 mm.). The thick yellow glass was submitted to short-path distillation (bath temperature 190–195° at 0.05–0.1 mm.). The yield of 2,2,2-trimethoxy-4-benzoyl5-phenyl-1,3,2-dioxaphospholene (XI) was 22 g. (94%).

Anal. Calcd. for $C_{18}H_{19}O_6P$: C, 59.7; H, 5.3; P, 8.6; mol. wt., 362. Found: C, 59.9; H, 5.5; P, 9.4; mol. wt., 312 (isothermal distillation in benzene).

The P^{31} n.m.r. spectrum had a 10-line signal at +49.3 ± 0.1 p.p.m. in CH_2Cl_2 *vs.* 85% H_3PO_4, J_{PH} = 13 c.p.s. The H^1 n.m.r. spectrum (in CCl_4) had $4H^1$ at τ 2.10, $6H^1$ at τ 2.71, and a $9H^1$ doublet at τ 6.42, J_{HP} = 13.5 c.p.s. The infrared spectrum (in CCl_4) had bands at: 6.08 (m), 6.29 (sh), 6.33 (ms), 6.45 (ms), 6.71 (m), 6.87 (sh), 6.92 (w), 7.55 (s), 7.66 (ms), 7.80 (m), 8.51 (ms), 8.70 (ms), 9.17 (sh), 9.26 (vs), 9.40 (vs), 9.90 (ms), and 11.3 (s) μ.

Reaction of Triisopropyl Phosphite with Diphenylpropanetrione (X).—A solution of the triketone (7.15 g.) in methylene chloride (20 ml.) was added dropwise to 18.7 g. (3 mole equiv.) of triisopropyl phosphite at 0–5° over a 1-hr. period with stirring under N_2. The orange-red color of the triketone turned pale yellow. The infrared spectrum showed complete reaction at this point. The solvent was removed at 20° (18 mm.), and the excess phosphite at 30° (0.5 mm.). The thick glass became crystalline on standing 1 hr. under pentane (10 ml., 0°). Filtration gave 7.5 g. of crystalline 2,2,2-triisopropoxy-4-benzoyl-5-phenyl-1,3,2-dioxaphospholene (XII) as yellow prisms, m.p. 46–48°. The mother liquid gave a second crop (4.0 g.) of the same material; yield, 87%.

Anal. Calcd. For $C_{21}H_{31}O_6P$: C, 64.6; H, 7.0; P, 7.0. Found: C, 64.2; H, 7.0; P, 7.0.

The P^{31} n.m.r. spectrum had a four-line signal at +54.9 ± 0.1 p.p.m. in CH_2Cl_2 *vs.* 85% H_3PO_4; J_{HP} = *ca.* 8 c.p.s. The H^1 n.m.r. spectrum (in CCl_4) had $4H^1$ at τ 2.1, $6H^1$ at τ 2.7, a $3H^1$ multiplet at τ 5.5, and an $18H^1$ doublet at τ 8.83 (at 60 Mc./sec., 2 c.p.s./sec.; 1 mm./c.p.s.). Expansion of the $18H^1$ doublet showed that it consisted of two doublets of equal intensities separated by 1 c.p.s.; both doublets with J_{HH} = 6.5 c.p.s. (at 0.2 c.p.s./sec. and 10 mm./c.p.s.).

The H^1 n.m.r. spectrum of triisopropyl phosphate, under comparable conditions gave a $3H^1$ multiplet at τ 5.5 and an $18H^1$ doublet at τ 8.75, J_{HH} = 6.5 c.p.s. This doublet consisted of two doublets of equal intensities separated by 1 c.p.s., like the adduct XII.

The infrared spectrum of the triketone–triisopropyl phosphite adduct XII had bands at 6.10 (m), 6.27 (sh), 6.33 (ms), 6.45 (ms), 6.71 (ms), 6.85 (w), 6.92 (w), 7.24 (ms), 7.55 (s), 7.66 (ms), 7.84 (ms), 8.55 (ms), 8.70 (ms), 9.09 (ms), 9.77 (vs), 10.00 (vs), and 10.30 (s) μ (in CCl_4).

The ultraviolet spectrum of XII had λ_{max} 346 mμ (ε 8000) and 250 mμ (ε 19,000).

Reaction of Trimethyl Phosphite with Phenylglyoxal. The preparation of 1:1 Adduct XIV.—Phenylglyoxal, obtained from Gallard-Schlessinger Co., was distilled (b.p. 90–93° at 15 mm.) and used immediately thereafter. A solution of phenylglyoxal (37.6 g.) in anhydrous methylene chloride (15 ml.) was added dropwise to trimethyl phosphite (140 g., 4 mole equiv.) at 0–5° under N_2 with good stirring over a period of 1 hr. The infrared spectrum of this solution did not change after 1 additional hr. at 20°. The solvent and the excess phosphite were removed below 60°, at 15 mm. and 0.1 mm., respectively. The residue was submitted to short-path distillation. Fraction 1 (10 g.) was collected up to 115° (0.3 mm., bath up to 150°). Fraction 2 (34.6 g., 48% of 1:1 adduct) was collected at 113–122° (0.2–0.3 mm., bath at 155°); this was the colorless liquid 2,2,2-trimethoxy-4-phenyl-1,3,2-dioxaphospholene (XIV), $n^{25}D$ 1.5308.

Anal. Calcd. for $C_{11}H_{15}O_5P$: C, 51.2; H, 5.8; P, 12.0; mol. wt., 258. Found: C, 50.7; H, 6.1; P, 12.3; mol. wt., 270 (isothermal distillation in benzene).

The P^{31} n.m.r. spectrum had a 20-line signal at +45.4 ± 0.1 p.p.m. in CCl_4 *vs.* 85% H_3PO_4, one J_{PH} = 32 c.p.s. and the second J_{PH} = 13 c.p.s. The H^1 n.m.r. spectrum (in CCl_4) had aromatic protons at τ 2.7, one doublet at τ 2.97, J_{HP} = 32 c.p.s.; this region integrated as $6H^1$. There was a $9H^1$ doublet at τ 6.40, J_{HP} = 13 c.p.s. Expansion in a scale of 10 mm./c.p.s. at a rate of 0.2 c.p.s./sec. showed only one doublet (60 Mc./sec.). The infrared spectrum (CCl_4) had bands at

(12) The shape of five-membered carbocyclic rings has been discussed by F. V. Brutcher, Jr., and W. Bauer [*J. Am. Chem. Soc.*, **84**, 2233 (1962)].

6.06 (m), 6.27 (vw), 6.71 (vw), 6.87 (w), 7.46 (w), 7.61 (w), 8.55 (m), 9.26 (vs), 9.43 (vs), and 10.8 (s) μ.

The H^1 n.m.r. spectrum in CD_3CN was identical with that in CCl_4.

Reaction of the Phenylglyoxal–Trimethyl Phosphite 1:1 Adduct XIV with Phenylglyoxal. The Preparation of Racemic and *meso*-2,2,2-Trimethoxy-4,5-dibenzoyl-1,3,2-dioxaphospholane (XV and XVI).—A solution of freshly distilled phenylglyoxal (3.29 g.) in methylene chloride (10 ml.) was added, dropwise over a 0.5-hr. period, to a solution of 1:1 adduct XIV (6.30 g.) in methylene chloride (10 ml.) at 0° under N_2. The clear solution was allowed to reach 20° and kept there 16 hr. (The infrared spectrum showed that the reaction was practically complete in 3 hr.) The solution was evaporated at 20° (20 mm., last traces at 1 mm.). The residue (*ca.* 9.6 g.) had one carbonyl band at 5.92 μ (CCl_4); the H^1 n.m.r. spectrum (CCl_4) had the signals due to the diastereomers XV and XVI in about 65:35 proportion (by integration); the P^{31} n.m.r. spectrum (CCl_4) had a multiplet at *ca.* 48 p.p.m. The mixture of isomers was kept at 10°, under pentane, for 2 days. The solvent was decanted, and the procedure was repeated with fresh pentane. The semisolid residue was dissolved in the minimum amount of hot benzene (1 ml./g.) The solution was diluted with an equal volume of hexane and then cooled to 10°. Crystals appeared within 2–3 days and were collected after 5 days. The *meso*-phenylglyoxal–trimethyl phosphite **2:1 adduct XV** was dried at 20° (0.2 mm.); yield, 2.0 g. (20%), m.p. 68–70°. *This material must be protected against moisture.* In other preparations, the yields were 20–30%.

Anal. Calcd. for $C_{19}H_{21}O_7P$: C, 58.2; H, 5.4; P. 7.9. Found: C, 58.3; H, 5.4; P, 7.9.

The P^{31} n.m.r. spectrum had a 30-line signal (18 detectable lines) at +46.9 ± 0.1 p.p.m. in CH_2Cl_2 *vs.* 85% H_3PO_4, J_{POCH} = 18 c.p.s. and J_{POCH_3} = 13 c.p.s. (Figure 4). The H^1 n.m.r. spectrum (CCl_4) had aromatic protons at τ 2.0 ($4H^1$) and 2.6 ($6H^1$), one $2H^1$ doublet at 4.50 (J_{HCOP} = 18.5 c.p.s.), and one $9H^1$ doublet at τ 6.56 (J_{H_3COP} = 12.8 c.p.s.). The infrared spectrum (CCl_4) had strong bands at 5.94 (C=O), 9.13, and 9.34 μ ($POCH_3$).

The benzene–hexane mother liquid, from which 20% of crystalline *meso*-XV had been removed, was evaporated. The H^1 n.m.r. spectrum of the residue showed *meso*-XV and racemic XVI, in about 55:45 proportion. The $2H^1$ doublet, J_{HP} = 18.7 c.p.s., due to the ring protons of the major isomer was at τ 4.50; the corresponding doublet, J_{HP} = 13.0 c.p.s., for the minor isomer was at τ 4.55. The $9H^1$ doublet, J_{HP} = 12.8 c.p.s., for the major methoxy was at τ 6.56, for the minor methoxy at τ 6.46 (J_{HP} = 12.8 c.p.s.). The infrared spectra of mixtures of XV and XVI of various compositions were very similar.

Reaction of the Biacetyl–Trimethyl Phosphite 1:1 Adduct II with Phenylglyoxal. Preparation of *cis*-XVII and *trans*-XVIII. 2,2,2-Trimethoxy-4β-methyl-4α-acetyl-5α-(and 5β-)benzoyl-1,3,2-dioxaphospholanes.—A solution of freshly distilled phenylglyoxal (2.68 g., 20 mmoles) in methylene chloride (10 ml.) was added, dropwise over a 15-min. period, to a solution of the biacetyl–TMP adduct (II, 4.2 g., 20 mmoles) in methylene chloride (10 ml.) at 0°, under dry N_2. After the exothermic reaction subsided, the stirred mixture was kept 2 hr. at 0°, and 40 hr. at 20° (the infrared spectra showed that most of the reaction had been completed in 1 hr.; there was a slight change within 2 hr. and no further changes after 16 and 40 hr.). The solvent was removed at 30° (first at 20 mm., then at 0.5 mm.). The pale yellow thick oil (6.5 g.) had equal carbonyl intensities at 5.82 and 5.90 μ. Both isomers XVII and XVIII were distinguishable by the strong doublet at τ 4.92 (J_{HP} = 18 c.p.s.) and the very weak doublet at τ 4.00 (J_{HP} = 23 c.p.s.). Short-path (*ca.* 1 in.) distillation at 0.2 mm., block temperature 150–155°, gave the mixture of isomers XVII and XVIII as a colorless, thick oil, $n^{25}D$ 1.5081. The yield was 75–80%.

Anal. Calcd. for $C_{15}H_{21}O_7P$: C, 52.3; H, 6.1; P, 9.0. Found: C, 52.1; H, 6.2; P, 8.8.

The P^{31} n.m.r. spectrum had a 20-line signal (16 detectable lines) at +50.1 ± 0.1 p.p.m. in CCl_4 *vs.* 85% H_3PO_4. The H^1 n.m.r. spectrum (CCl_4) had aromatic protons at τ 2.1 ($2H^1$) and 2.6 ($3H^1$); one $1H^1$ doublet at τ 4.95 (J_{HP} = 18.6 c.p.s.), another at τ 4.03 (J_{HP} = 22.3 c.p.s., integration proportion 85:15), one $9H^1$ doublet at τ 6.50 (J_{HP} = 12.7 c.p.s.), another at τ 6.42 (J_{HP} = 12.7 c.p.s.), a $3H^1$ singlet at τ 7.75 which could not be resolved at 60 Mc.p.s., one $3H^1$ singlet at τ 8.54, and another at τ 8.95 (integration proportion 85:15); the integration of the acetyl *vs.* the two methyl signals showed that the acetyls of the major and the minor isomers coincided. The infrared spectrum (CCl_4) had strong bands at 5.74 and 5.92 μ (equal intensities), very strong bands at 9.16 and 9.40 μ, weak bands at 6.27 and 6.35 μ, and medium bands at 6.90, 7.41, 8.15, and 8.50 μ.

Other experiments in which a 5 *M* solution of phenylglyoxal (6.34 g.) in methylene chloride was added to a 5 *M* solution of biacetyl–TMP adduct II (9.87 g.) at 0° gave about 80% of distilled isomer mixture XVII and XVIII in the same proportion. When the phenylglyoxal was added to the adduct II at 0° over a 5-min. period *in the absence of solvent*, the same proportion of isomers XVII and XVIII resulted.

Reaction of the Phenylglyoxal–Trimethyl Phosphite 1:1 Adduct XIV with Biacetyl. Formation of *cis*-XVII and *trans*-XVIII.—Biacetyl (XIX, 1.04 g., 12.0 mmoles) and the aldehyde adduct XIV (1.04 g., 4.0 mmoles) were mixed at 20° under N_2. There was no evidence of reaction. Infrared spectra of aliquots were taken after 1, 4, 6, and 8 days. Reaction was nearly complete after 8 days. The H^1 n.m.r. spectrum showed the *cis*-XVII and the *trans*-XVIII isomers in a 60:40 proportion, by integration of the ring-proton doublets and of the ring-methyl singlets.

When the reagents were mixed in equimolar amounts, the reaction was still incomplete after 38 days.

A 2-*M* solution of the reagents (biacetyl and XIV, equimolar) in methylene chloride had considerable amounts of unreacted biacetyl after 13 days. The isomers XVII and XVIII were formed also in a 60:40 proportion under these conditions.

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