Methyl 1,7,8,11,12,12-Hexachlorohexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecane-2-carboxylate (10).—Two 25-g batches (0.118 mole in total) of **9** in 500 ml of acetone each were irradiated for 1 hr, and the resulting solutions were combined and evaporated. Recrystallization of the residue from methanol gave 41.5 g (83%) of **10**: mp 165–167°; infrared absorption at 5.77 μ (C═O); nmr signals ($CDCl_3$) at δ 1.78 (2 H AB pattern, J = 11.5 cps, $\delta_A - \delta_B$ = 17 cps, 4-CH_2), 3.15 and 3.9 (partially resolved multiplets, 4 H and 1 H, respectively, methine CH), and 3.77 (3 H singlet, OCH_3).

Anal. Calcd for $C_{14}H_{10}Cl_6O_2$: C, 39.75; H, 2.38, mol wt, 423. Found: C, 39.99; H, 2.27; mol wt (osmometric), 426.

1,7,8,11,12,12-Hexachlorohexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecane-2-carboxylic Acid (11).—Compound **10** (30 g, 0.0709 mole) was refluxed for 32 hr with 400 ml each of ethanol and 2.5 *N* aqueous NaOH. The resulting clear solution was evaporated to *ca.* 300 ml, diluted with 600 ml of water, and acidified with HCl to precipitate 28.3 g (98%) of **11**, suitable for use in the next step. Recrystallization from ethyl acetate–hexane gave material which darkened but did not melt below 350°; infrared absorptions at 3.75 (broad, OH) and 5.87 μ (C═O); nmr signals (pyridine)[20] at δ 1.79 (2 H AB pattern, J = 11.5 cps, $\delta_A - \delta_B$ = 31.5 cps, 4-CH_2) and 3.14, 3.41, and 4.22 (3 H, 1 H, and 1 H, respectively, partially resolved multiplets, methine CH).

Anal. Calcd for $C_{13}H_8Cl_6O_2$: C, 38.18; H, 1.97. Found: C, 38.16; H, 2.00.

1,7,8,11,12,12-Hexachlorohexahydro[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]-dodecan-2-amine (12).—Compound **11** (20 g, 0.0489 mole) was subjected to the Curtius reaction sequence exactly as in the conversion of **5** to **6**. In this case both the acid chloride (C═O absorption at 5.71 μ) and the isocyanate (N═C═O absorption at 4.42 μ) were crystalline solids. The yield of **12** precipitated at pH 9 was 14.0 g (75%), suitable for use in the next step. Recrystallization from ethanol–water gave material which darkened but did not melt below 350°; infrared absorptions at 2.95, 3.01, and 6.17 μ (NH_2); nmr signals (CF_3COOH) at δ 2.24 (2 H AB pattern, J = 12.5 cps, $\delta_A - \delta_B$ = 28 cps, 4-CH_2), 3.1–3.8 (5 H as overlapping broad singlet and partially resolved multiplet, methine CH), and 7.8 (3 H hump, —NH_3^+).

Anal. Calcd for $C_{12}H_9Cl_6N$: C, 37.93; H, 2.39; N, 3.69. Found: C, 38.18; H, 2.38; N, 3.48.

Hexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecan-2-amine (13).—A 14.0-g (0.0368 mole) sample of **12** was dehalogenated and the product purified[23] by the procedure which was used for the conversion of **6** to **7**. Three recrystallizations were required to give hexamate (5 g) of 99% purity. This yielded 1.45 g (19%) of the **hydrochloride** of **13**: darkens and shrinks but does not melt below 350°; infrared absorptions at 3.9 (multiplet), 4.96, 6.20, and 6.30 μ (NH_3^+); nmr signals (D_2O–DCl)[24] at δ 1.78 (4 H AB pattern, J = 11 cps, $\delta_A - \delta_B$ = 30 cps, 4- and 12-CH_2), and 2.53 and 2.66 (9 H as two overlapping broad singlets, methine CH); pK_a (water, 25°), 9.69.

Anal. Calcd for $C_{12}H_{16}ClN$; C, 68.72; H, 7.69; Cl, 16.91; N, 6.68. Found: C, 68.88; H, 7.80; Cl (ionic), 16.62; N, 6.65.

Registry No.—**3**, 14128-62-2; **4**, 14154-65-5; **5**, 14128-63-3; **6**, 14171-90-5; hydrochloride of **7**, 14128-64-4; **8**, 14128-65-5; **9**, 14171-91-6; **10**, 14128-66-6; **11**, 14128-67-7; **12**, 14128-68-8; hydrochloride of **13**, 14128-69-9.

Acknowledgments.—We wish to thank Dr. J. R. E. Hoover for his interest and encouragement during the course of this work and Mr. J. J. Taggart for his skilled and cheerful technical assistance. We are indebted to Miss M. A. Carroll and her associates for the microanalytical data, Dr. W. E. Thompson and his staff for the nmr spectra, Mr. J. W. Lockard for the gas chromatograms, and Mr. J. W. Hamill for the pK_a determinations.

Molecular Rearrangements during Solvolyses of Pentaoxyphosphoranes. Polyketones Derived from Phthalaldehyde and Terephthalaldehyde[1]

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Methanolysis of the trimethylbiacetyl–benzaldehyde–phosphite adduct (2,2,2-trimethoxy-4β-methyl-4α-acetyl-5α-phenyl-1,3,2-dioxaphospholane) gave trimethyl phosphate and 3-phenyl-2,4-pentanedione. This new type of molecular rearrangement involved the 1,2 shift of an acetyl group during the loss of phosphate. 1-Phenyl-2-acetylpropylene oxide was not an intermediate in the rearrangement. The bispentaoxyphosphorane derived from the reaction of two molecules of 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene with phthalaldehyde gave two molecules of trimethyl phosphate and one molecule of 1,2-bis(diacetylmethyl)benzene. This tetraketone was obtained in the dienol diketo and the monoenol triketo tautomers. The bispentaoxyphosphorane, made from two molecules of 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene and one molecule of terephthalaldehyde, underwent methanolysis to trimethyl phosphate and 1,4-bis(diacetylmethyl)benzene, which was obtained as the dienol diketo tautomer. The corresponding 1,2-bis-4′- and 1,4-bis-4′-(3′,5′-dimethyl)pyrazolylbenzene were made from the tetraketones and hydrazine.

The nucleophilic addition of 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene, I, to the carbonyl function of benzaldehyde gave the two diasteromeric forms of 2,2,2-trimethoxy-4-methyl-4-acetyl-5-phenyl-1,3,2-dioxaphospholane,[3] II. The isomers IIa and IIb with the *cis*- and *trans*-CH_3/H configurations were formed in about 90:10 proportion, respectively. The pentavalency of the phosphorus was based on the large positive value of the P^{31} nmr shift.[4] The configurations were assigned from the H^1 nmr data.

The condensation of two molecules of the phospholene I with phthalaldehyde gave the three possible diastereomers of a bispentaoxyphosphorane,[5] IIIa,

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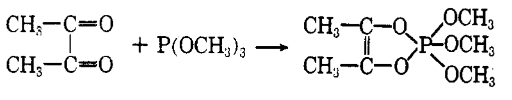
(1) (a) Organic Compounds with Pentavalent Phosphorus, part XXXI; (b) part XXX, F. Ramirez, M. Nagabhushanam, and C. P. Smith, *Tetrahedron*, **23**, (1967); (c) part XXIX, F. Ramirez, S. B. Bhatia, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 3030 (1967).

(2) This investigation was supported by Public Health Service Grant CA-04769-08 from the National Cancer Institute, and by the National Science Foundation, Grant GP 6690-Y.

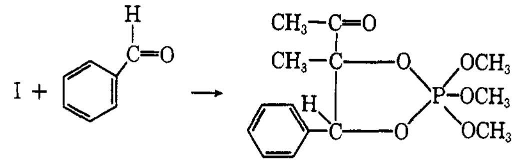
(3) F. Ramirez, N. Ramanathan, N. B. Desai, C. V. Greco, and S. R. Heller, *J. Am. Chem. Soc.*, **87**, 543 (1965).

(4) (a) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *ibid.* **87**, 127 (1965); (b) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, **89**, 2268 (1967).

(5) F. Ramirez, S. B. Bhatia, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **32**, 2194 (1967).

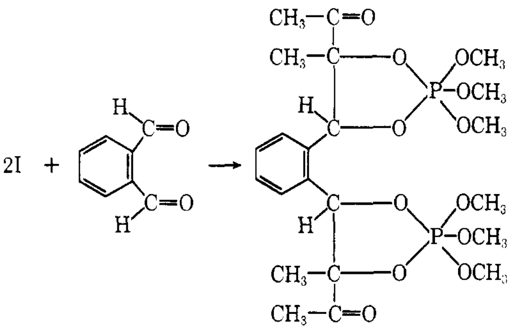


I, δ P^{31} + 48.9 ppm *vs.* 85% H$_3$PO$_4$



IIa, *cis*-CH$_3$/H; δ P^{31} + 51.5 ppm
b, *trans*-CH$_3$/H

IIIb, and IIIc, in the approximate proportions 30:60:10. The isomers IIIa and IIIb were obtained in pure form by fractional crystallization.



IIIa, *cis*-H/CH$_3$, *cis*-H/CH$_3$; δ P^{31} + 49.3 ppm
b, *cis*-H/CH$_3$, *trans*-H/CH$_3$; δ P^{31} + 49.5 ppm
c, *trans*-H/CH$_3$, *trans*-H/CH$_3$

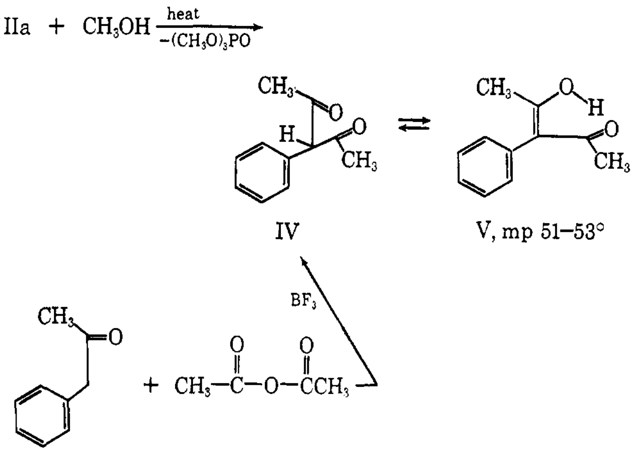
The liquid oxyphosphoranes, II, could be distilled unchanged under reduced pressure. The crystalline oxyphosphoranes, III, also showed considerable thermal stability. However, the oxyphosphoranes appeared to be quite sensitive to methanol. This paper is concerned with the alcoholysis of these compounds. The preparation and the alcoholysis of pentaoxyphosphoranes derived from the reaction of the phospholene I with terephthaladehyde were also investigated.

Results

The trimethylbiacetyl–benzaldehyde–phosphite adducts, IIa and IIb, readily lost trimethyl phosphate when treated with hot methanol. The other product of this reaction was the enol form, V, of 3-phenyl-2,4-pentanedione, IV. This substance V had the typical infrared band associated with conjugate chelation of the enol form of β-diketones. The H^1 nmr spectrum gave a 6 H^1 singlet at τ 8.20; the equivalency of the two methyl groups is presumably due to a relative rapid proton exchange among the two carbonyl functions of the symmetric diketone.[6] The spectrum had a 1 H^1 singlet at τ −7.17 due to the acidic proton of the enol.

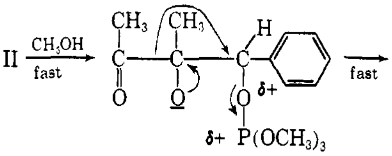
An authentic sample of the enol V was prepared from methylbenzyl ketone and acetic anhydride by the procedure of Adams and Hauser.[7]

Evidently, a rearrangement of the carbon skeleton occurred as a result of the solvolysis of the pentaoxyphosphorane. It became of interest to determine if the rearrangement occurred during the loss of trimethyl phosphate, or whether the loss of phosphate resulted in the formation of an epoxide, VI. The acid-catalyzed, 1,2 shift of the acetyl group of α keto epoxides has been thoroughly investigated.[8] To test this point, an authentic sample of one of the diastereomers of 1-phenyl-2-acetylpropylene oxide, VI, was made from 3-chloro-2-butanone and benzaldehyde.[9] This α keto epoxide was recovered unchanged when its solution in methanol was kept 6 hr at reflux temperature. Even when 25 mole % of phosphoric acid was added to a 1 *M* solution of the epoxide, VI, in methanol, the molecular rearrangement to the β-diketone, IV, was quite slow. The rearrangement proceeded to approximately 23% after 24 hr at reflux temperature. It appears then, that the conversion of the pentaoxyphosphorane, II, to the enol, V, by methanol occurred during the loss of the phosphate. The driving force of the rearrangement could be the loss of the phosphate with the incipient formation of a benzyl carbonium ion, as shown in formula VII.

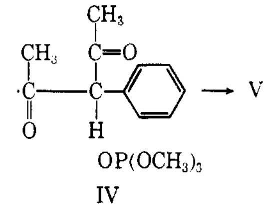


IV

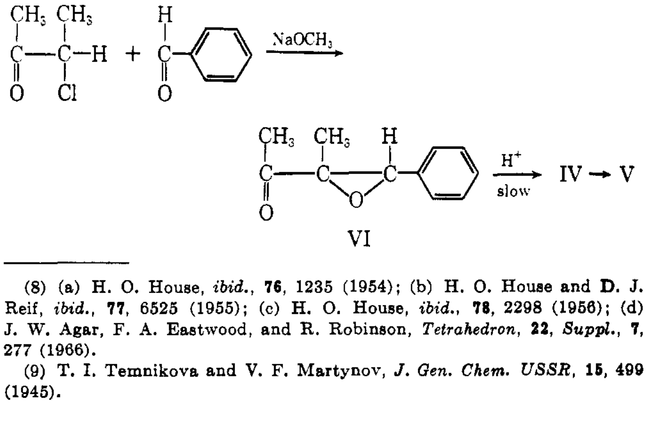
V, mp 51–53°



VII



IV



VI

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[6] (a) S. Forsen, *Acta Chem. Scand.*, **18**, 513 (1964); (b) *ibid.*, **18**, 1209 (1964).

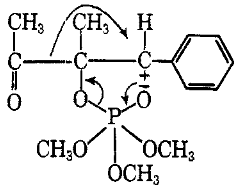
[7] J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **67**, 284 (1945).

[8] (a) H. O. House, *ibid.*, **76**, 1235 (1954); (b) H. O. House and D. J. Reif, *ibid.*, **77**, 6525 (1955); (c) H. O. House, *ibid.*, **78**, 2298 (1956); (d) J. W. Agar, F. A. Eastwood, and R. Robinson, *Tetrahedron*, **22**, *Suppl.*, **7**, 277 (1966).

[9] T. I. Temnikova and V. F. Martynov, *J. Gen. Chem. USSR*, **15**, 499 (1945).

This mechanism involves a P–O bond fission in the oxyphosphorane. Such a process results in considerable charge separation and is, therefore, consistent with the observation that the rearrangement occurred best in a solvent of relatively high dielectric constant, such as methanol. Indeed, the behavior of the biacetyl–benzaldehyde–phosphite adduct, II, in boiling xylene differed significantly from its behavior in boiling methanol. In the aprotic solvent an isomerization of the *cis*-CH_3/H isomer, IIa, to the *trans*-CH_3/H isomer, IIb, was noted. The course of the isomerization was followed by H^1 nmr spectrometry, and there was little evidence for the formation of trimethyl phosphate. This isomerization could involve a partial dissociation of the adduct into the original reactants followed by recombination. The ratio of diastereomers originally produced in the condensation of the phospholene with the aldehyde, therefore, need not represent the only ratio obtainable under different experimental conditions.

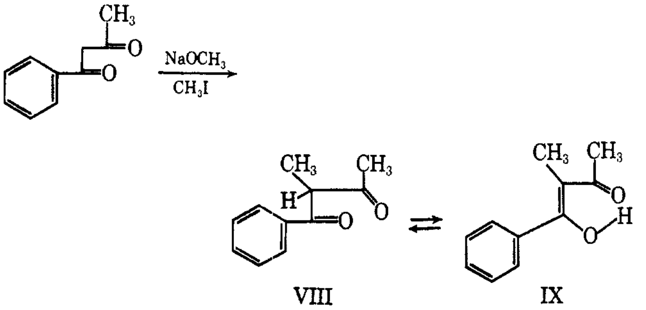
Intermediate VII is not the only reasonable path for the conversion of the oxyphosphorane, II, to the enol, V. For example, a C–O bond fission in the oxyphosphorane could produce intermediate VIIa, which would then give rise to the products as indicated in the formula.



VIIa

Bissing and Speziale[10] have reported the isomerization of simple epoxides to ketones and aldehydes by tertiary phosphine oxides at 160°. We, therefore, investigated the effect of trimethyl phosphate on the α ketoepoxide, VI, in boiling methanol. No reaction was observed after 1 hr while the rearrangement of the oxyphosphorane, II, to the enol, V, was complete within 30 min in boiling methanol.

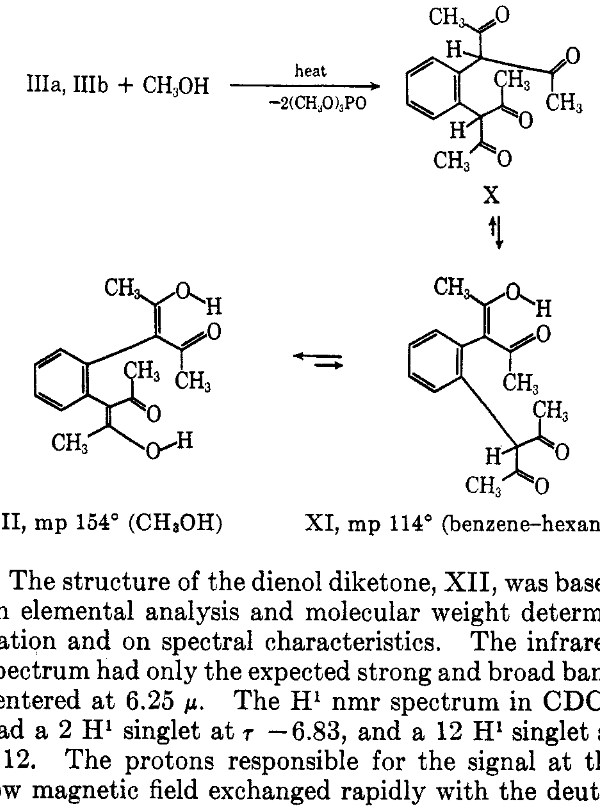
The product of the methanolysis of the trimethyl-biacetyl–benzaldehyde–phosphite adduct, II, had been incorrectly formulated as the enol form IX of 1-phenyl-2-methyl-1,3-butanedione,[3] VIII. In other words,



VIII IX

the loss of trimethyl phosphate from II was erroneously assumed to proceed by a simple elimination without a rearrangement of the carbon skeleton.[1] An authentic sample of the diketone VIII was made from sodiobenzoyl acetone and methyl iodide.[11] The substance thus prepared existed in aprotic solvents as the diketone almost exclusively. The infrared spectrum had two carbonyl absorptions at 5.80 and 5.95 μ due to the acetyl and the benzoyl groups, respectively. The H^1 nmr spectrum had a 3 H^1 doublet at τ 8.60, J_{HH} = 7.0 cps, due to the methyl groups coupled with the methine proton. The latter gave a quartet at τ 5.38. The protons of the acetyl group gave a singlet at τ 7.88.

The methanolysis of the *cis,cis* and the *cis,trans* isomers IIIa and IIIb, of the bisoxyphosphorane derived from the phospholene I and phthalaldehyde occurred smoothly. Two molecules of trimethyl phosphate were lost and a molecular rearrangement occurred to the symmetrical bis-β-diketone, X. This tetraketone was obtained in two crystalline forms, the enol triketone, XI, and the dienol diketone, XII.



X

XII, mp 154° (CH_3OH) XI, mp 114° (benzene–hexane)

The structure of the dienol diketone, XII, was based on elemental analysis and molecular weight determination and on spectral characteristics. The infrared spectrum had only the expected strong and broad band centered at 6.25 μ. The H^1 nmr spectrum in $CDCl_3$ had a 2 H^1 singlet at τ −6.83, and a 12 H^1 singlet at 8.12. The protons responsible for the signal at the low magnetic field exchanged rapidly with the deuterium of D_2O. However, the protons responsible for the signal at high magnetic field did not exchange with D_2O.

The monoenol triketone, XI, had a strong band at 5.85 μ with a shoulder at 5.80 μ due to the carbonyl functions of the β-diketone. The spectrum had a second strong band centered at 6.25 μ associated with the chelated enol portion of a molecule. The H^1 nmr spectrum had a 1 H^1 singlet at τ −6.78; this H^1 rapidly exchanged with D_2O. The spectrum had a 1 H^1 singlet at τ 4.90; this H^1 did not exchange readily with D_2O. The six protons of the two acetyl groups gave a singlet at τ 7.83 and the six protons of the two methyl groups involved in the enol portion gave a singlet at 8.20. The latter two did not exchange readily with D_2O.

Both tautomers, XI and XII, reacted with hydra-

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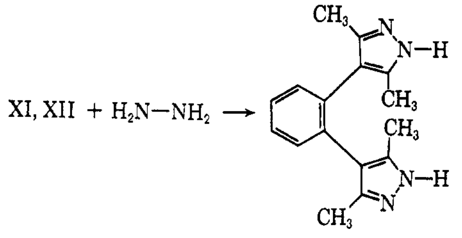
[10] D. E. Bissing and A. J. Speziale, *J. Am. Chem. Soc.*, **87**, 1405 (1965).

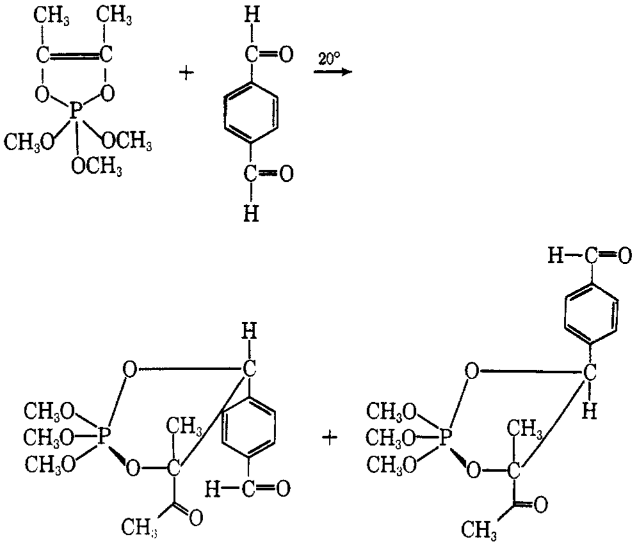
[11] (a) W. Dieckman, *Ber.*, **45**, 2685 (1912); (b) K. Auwers and H. Jacobson, *Ann.*, **426**, 161 (1922); (c) C. Weygand, *Ber.*, **61B**, 687 (1928).

zine and gave the same high melting 1,2-bis-4′-(3′,5′-dimethyl)pyrazolylbenzene, XIII.



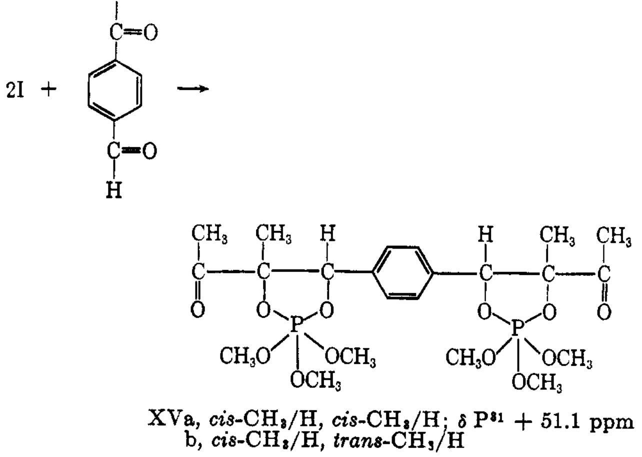
XIII

The reaction of the phospholene I with terephthalaldehyde could be carried out stepwise as in the case of *o*-phthalaldehyde. Two diastereomers, XIVa and XIVb, were produced, but only the major isomer XIVa was obtained in crystalline form. The structure and the configuration were based on the P^{31} and H^1 nmr data.



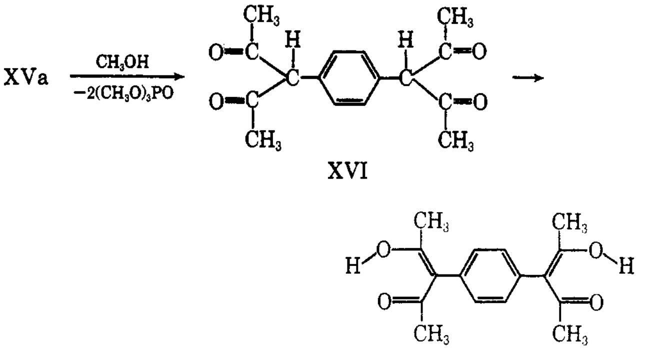
XIVa, *cis*-CH_3/H; δ P^{31} + 51.2 ppm XIVb, *trans*-CH_3/H

The reaction of 2 moles of the phospholene I with 1 mole of terephthalaldehyde gave two of the three possible diastereomers of the bispentaoxyphosphorane, XVa and XVb. The *cis,cis*-CH_3/H isomer was isolated in pure crystalline form. The P^{31} nmr shift was as expected for a pentaoxyphosphorane. The H^1 nmr spectrum gave a 2 H^1 doublet, J_{HP} = 4.0 cps at τ 5.32 attributed to the two equivalent methine protons coupled with the phosphorus nucleus. The spectrum had an 18 H^1 doublet, J_{HP} = 12.8 cps, at τ 6.30 due to the two sets of three methoxy groups which are magnetically equivalent. There was a 6 H^1 singlet at τ 8.30 and a 6 H^1 singlet at 8.40, which were attributed respectively to the two magnetically equivalent acetyl groups and methyl groups on the phospholane ring.



XVa, *cis*-CH_3/H, *cis*-CH_3/H; δ P^{31} + 51.1 ppm
b, *cis*-CH_3/H, *trans*-CH_3/H

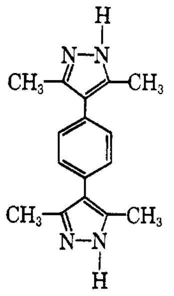
The methanolysis of the *cis,cis* isomer, XVa, proceeded with the loss of two molecules of trimethyl phosphate and involved a molecular rearrangement, XVa → XVI, analogous to that observed in the case of the *o*-phthalaldehyde adduct, III. In this case, only the dienol diketo tautomer, XVII, was obtained in crystalline form. The infrared spectrum had one strong carbonyl band centered at 6.25 μ. The H^1 nmr spectrum had the acidic 2 H^1 at τ −6.60 and the 12 H^1 singlet at 8.08. No tautomerization was observed even under the action of triethylamine.



XVI

XVII

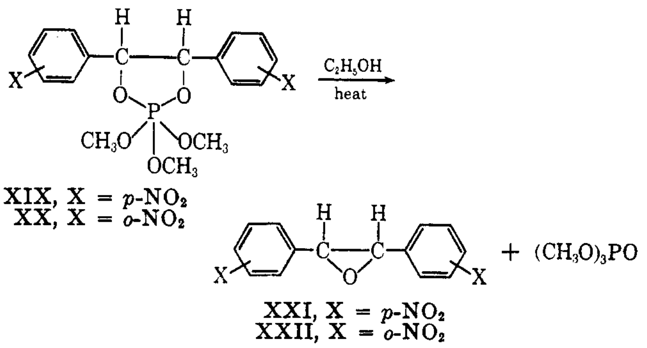
Reaction of the dienol diketone, XVII, with hydrazine gave the high melting 1,4-bis-4′-(3′,5′-dimethyl)-pyrazolylbenzene, XVIII.



XVIII

Discussion

The methanolysis of 2,2,2-trialkoxy-1,3,2-dioxaphospholanes having *two hydrogen atoms and two phenyl groups* on the phospholane ring, like XIX and XX,

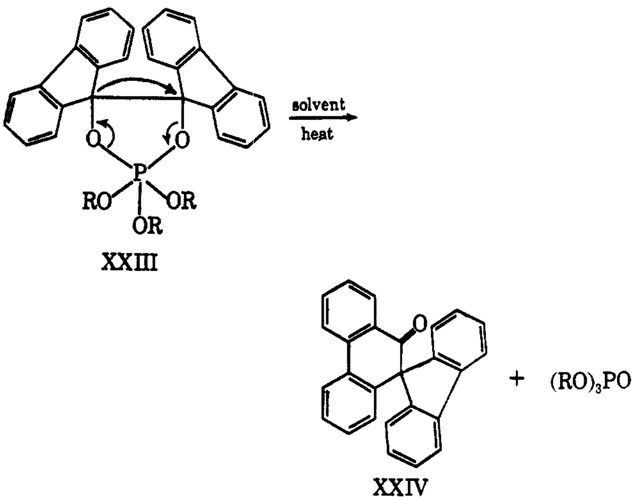


XIX, X = *p*-NO_2
XX, X = *o*-NO_2

XXI, X = *p*-NO_2
XXII, X = *o*-NO_2

resulted in the loss of trialkyl phosphate and the formation of an epoxide,[12] XXI, and XXII.

When the dioxaphospholane was derived from a suitably constituted monoketone, for example fluorenone, a different behavior was observed upon heating in a variety of solvents. The 2:1 fluorenone–trialkyl phosphites, XXIII, underwent a pinacolic type of rearrangement to 9-diphenylenephenanthrone,[13] XXIV.

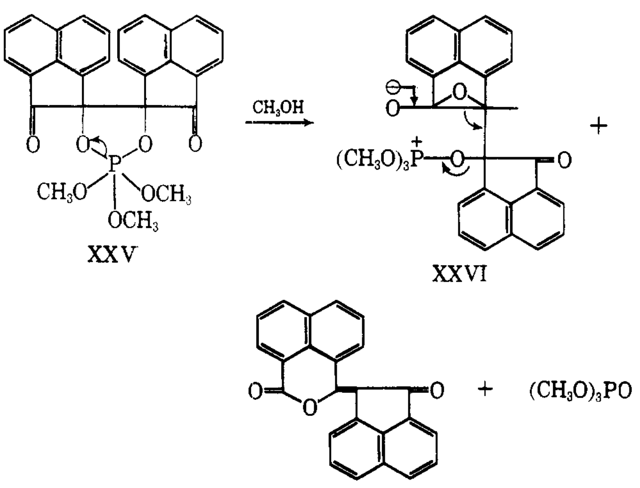


XXIII

XXIV

The phospholane, XXIII, varied greatly in thermal stability. The fluorenone–triisopropyl phosphite adduct decomposed into the phenanthrone, XXIV, and triisopropyl phosphate in boiling benzene, but the corresponding adduct from triethyl phosphite and trimethyl phosphite were stable under comparable conditions. In boiling diglyme, all the adducts decomposed into the corresponding phosphates and phenanthrone, XXIV. These rearrangements competed with some dissociation of the phosphorane, XXIII, into fluorenone and the trialkyl phosphite.

A third type of behavior has been observed when certain pentaoxyphosphoranes were heated in solvents. Thus, the oxyphosphorane, XXV, prepared from acenaphthenequinone and trimethyl phosphite was converted by methanol into the lactone of the enol form of a β-diketone, XXVII. The intermediate, XXVI, was suggested for this rearrangement.[14]

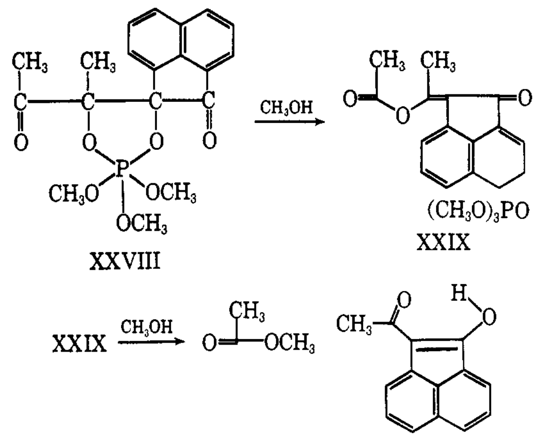


XXV

XXVI

XXVII

This type of molecular rearrangement appears to be quite general and was observed also in the case of the oxyphosphorane, XXVIII, derived from the reaction of the phospholene I with acenaphthenequinone. Now the products were methyl acetate, and the enol form of the β-diketone, XXX, in addition to trimethyl phosphate. These products were formed presumably by solvolysis of the intermediate enol acetate,[14] XXIX.

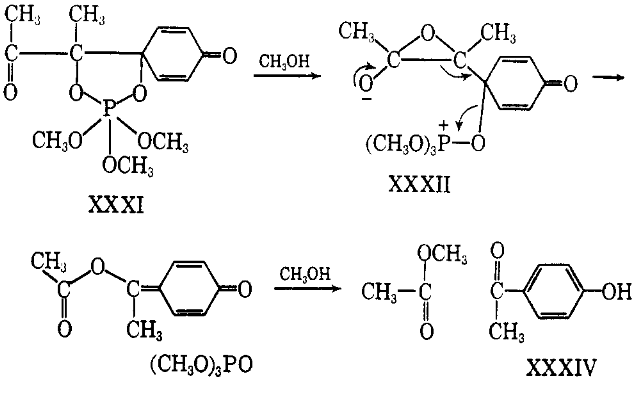


XXVIII

XXIX

XXX

A related rearrangement occurred during the methanolysis of the oxyphosphorane, XXXI, derived from the reaction of the phospholene, I, with p-benzoquinone.[15] The products now were methyl acetate, p-hydroxyacetophenone (XXXIV), and trimethyl phosphate. These could originate through an intermediate enol acetate, XXXIII.



XXXI

XXXII

XXXIII

XXXIV

The course of the solvolytic and the thermal decomposition of the pentaoxyphosphoranes depend a great deal on the stereoelectronic characteristics of the molecule. However, it is clear that the departure of the trialkyl phosphate ester from a pentaoxyphosphorane provides a strong driving force. This can manifest itself in the form of molecular rearrangements or as substitution reactions leading to epoxides.

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Experimental Section

Analyses were performed by Schwarzkopf Analytical Laboratories, Woodside, N. Y. The P^{31} nmr values are given in parts per million (ppm) *vs.* 85% H_3PO_4, taken at 40.5 Mc/sec. The H^1 nmr shifts are given in parts per million from TMS = 10 (τ values), taken in a Varian A-60 instrument.

Preparation of the Trimethyl Biacetyl–Benzaldehyde–Phosphite Adducts, IIa and IIb. Interconversion of Diastereomers IIa $\rightleftarrows$ IIb.—The reaction of 1 mole of the biacetyl–trimethyl phosphite adduct, I, with 3 moles of benzaldehyde was carried out at 20° as described.[3] The liquid obtained after short-path distillation was shown to contain the two diastereomers, *cis*-CH_3/H, IIa, and *trans*-CH_3/H, IIb, in *ca.* 90:10 proportion by H^1 nmr spectrometry. The above mixture of isomers (6.5 g) was dissolved in xylene (50 ml) and the solution was kept 12 hr at reflux temperature. The H^1 nmr spectrum showed that some of the *cis* isomer, IIa, had been converted into the *trans* isomer, IIb. The proportion of isomers was 40:60 *cis*: *trans*. The H^1 nmr signals due to the minor isomer, IIa, were at τ 8.30 (acetyl *cis* to phenyl) and at 8.40 (methyl *cis* to H). The signals due to the major isomer, IIb, were at τ 7.65 (acetyl *cis* to H) and at 9.12 (methyl *cis* to phenyl).

After 42 hr at the reflux temperature of xylene, the proportion of *cis*: *trans* isomers was *ca.* 30:70.

Methanolysis of the *cis*-CH_3/H Trimethyl Biacetyl–Benzaldehyde–Phosphite Adduct, IIa.—A solution of the diasteromer IIa (*cis*-CH_3/H) in anhydrous methanol was kept 30 min at reflux temperature. The product of the reaction was isolated as described.[3] The colorless oil was purified by short-path distillation (bp 65–75°, 0.2 mm); it solidified on standing and was obtained as crystals, mp 53–54° from hexane. The infrared spectrum had a broad and strong band centered at 6.25 μ (CCl_4). The H^1 nmr spectrum (CCl_4) had a 1 H^1 signal at τ − 7.17, a 5 H^1 signal at 2.5, and a 6 H^1 signal at 6.20. The spectrum was similar in $CDCl_3$ and in benzene. The 6 H^1 signal could not be resolved at 60 or at 100 Mc/sec. This substance was identical with a sample of 3-phenyl-3-penten-4-ol-2-one, V (enol form of 3-phenyl-2,4-pentadione, IV). The latter was prepared from methyl benzyl ketone and acetic anhydride by the procedure of Adams and Hauser.[7]

The structure of 3-methyl-4-phenyl-3-buten-4-ol-2-one, IX, (enol form of 1-phenyl-2-methyl-1,3-butanedione, VIII) previously assigned[3] to the methanolysis product was shown to be in error. An authentic sample of the diketo form VIII was made from sodiobenzoyl acetone and methyl iodide as described.[11] The infrared spectrum (CH_2Cl_2) has strong bands at 5.80 (acetyl) and 5.85 μ (benzoyl). The H^1 nmr spectrum ($CDCl_3$) had a 5 H^1 multiplet at τ 2.1 and 2.5 (aromatic protons), a 1 H^1 quartet (J_{HH} = 7.0 cps) at 5.38 (methine proton), a 3 H^1 singlet at 7.88 (acetyl) and a 3 H^1 doublet (J_{HH} = 7.0 cps) at 8.60 (methyl coupled with methine protons).

Methanolysis of the Bisdioxaphospholanes, IIIa and IIIb, Made from Two Moles of 2,2,2-Trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene, I, and One Mole of *o*-Phthalaldehyde.—A crystalline mixture of the *cis,cis* IIIa and the *cis,trans* IIIb isomers of the bisdioxaphospholane was prepared as described[5] from the reaction of the dioxaphospholene, I, with *o*-phthalaldehyde. A 50:50 crystalline mixture of the diastereomeric bisdioxaphospholanes, IIIa and IIIb (6.0 g), was suspended in methanol (50 ml) and kept for 1 hr at reflux temperature. The clear solution was evaporated at 20° (20 mm). The residue became partly crystalline after 12 hr at 20°. The crystals (1.0 g, 35%) were of the dienol diketo form, XII, of 1,2-bis(diacetylmethyl)benzene, X. The analytical sample, XII, obtained after one crystallization from methanol and one from benzene–hexane, had mp 154–155°.

Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.1; H, 6.6; mol wt, 274. Found: C, 69.4; H, 6.7; mol wt, 244 (cryoscopic in benzene).

The spectral properties of the dienol diketone, XII, were obtained on a *freshly recrystallized sample in fresh solutions.* The infrared spectrum (CH_2Cl_2) had a broad and strong band from 6.1 to 6.5, centered at 6.25, and bands at 7.15, and 7.55 μ. No band was present between 5.5 and 6.0 μ.

The H^1 nmr spectrum of a 0.53 *M* solution of the dienol diketone, XII, in $CDCl_3$ had a 4 H^1 multiplet at τ 2.6 (aromatic), a 2 H^1 singlet at −6.83 (enol protons), and a 12 H^1 singlet at 8.12 (four nonresolvable methyl groups). The signal due to the methyl protons could not be resolved in benzene solution.

The protons responsible for the signal at τ −6.83 in $CDCl_3$ solution exchanged rapidly with deuterium oxide. In this experiment, 0.2 ml of D_2O was added to a solution of 731 mg of dienol diketone, XII, in 5 ml of $CDCl_3$; the spectrum was examined after 30 min, 3 hr, and 24 hr.

The protons responsible for the signal at τ 8.12 did not exchange with deuterium oxide under the conditions described above.

The filtrate from which 35% of the dienol diketone, XII, had been removed was distilled at 0.05 mm; the distillate was shown to be trimethyl phosphate.

The residue from the distillation contained a mixture of products. The main constituents were the dienol diketone, XII, and its tautomer, the monoenol triketone, XI (*vide infra*).

The methanolysis of pure crystalline *cis,cis* (IIIa) or *cis,trans* (IIIb) isomers gave mixtures of the dienol diketone, XII, and the monoenol triketone, XI, as shown by H^1 nmr spectrometry.

Direct Conversion of Phthalaldehyde and Biacetyl to the Dienol Diketone, XII, by Means of Trimethyl Phosphite and Methanol.—The condensation of biacetyl with trimethyl phosphite to give the dioxaphospholene, I, was carried out as described.[3] Then, 2 mole equiv (34.5 g) of I was added to a solution of *o*-phthalaldehyde (10.5 g) in methylene chloride (40 ml); the solution was stirred 3 days at 20°. The solvent was removed at 20° (20 mm) and the residue was dissolved in methanol (100 ml). The solution was kept 2 hr at reflux temperature. The solvent was removed at 20° (20 mm). The residue became partly crystalline at 20° within 20 hr; the first crop (2.5 g) of dienol diketone, XII, was filtered. The filtrate was freed from trimethyl phosphate at a bath temperature of 85° (0.05 mm). The residue was crystallized from benzene (35 ml) and hexane (15 ml) and gave more (3.8 g) of dienol diketone, XII; yield of crystalline XII, 30%. The filtrate was evaporated to dryness; the infrared and H^1 nmr spectra of the noncrystalline residue showed the presence of more dienol diketone, XII, and the tautomeric monoenol triketone, XI.

Equilibration of the Dienol Diketone, XII, with the Monoenol Triketone, XI.—A solution of the crystalline dienol diketone, XII (2.4 g), in methanol (40 ml) was kept for 20 hr at reflux temperature. The clear yellow solution was concentrated to one-half of its original volume, when crystals separated. The infrared and the H^1 nmr spectra of this material (400 mg, melting range 96–115°) corresponded to a mixture of unchanged dienol diketone, XII, and its tautomer, the monoenol triketone, XI. The methanol filtrate was evaporated to dryness; the residue was crystallized from benzene–hexane giving monoenol triketone, XI (430 mg), melting in the range 104–117°. Another crystallization from benzene–hexane raised the melting point of XI to 114–116°.

Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.1; H, 6.6. Found: C, 69.7; H, 6.5.

The infrared spectrum (CH_2Cl_2) had a broad band from 6.1 to 6.5 μ centered at 6.25 and *a stronger band at* 5.85 with a strong shoulder at 5.80 μ.

The H^1 nmr spectrum of a 1.27 *M* solution of the monoenol triketone, XI, in $CDCl_3$ had a 4 H^1 multiplet at τ 2.6 (aromatic), a 1 H^1 singlet at −6.78 (enol protons), a 1 H^1 singlet at 4.90 and a 6 H^1 singlet at 7.83 (acetyls), and a 6 H^1 singlet at 8.20 (methyls). The spectrum did not change significantly when the $CDCl_3$ solution was diluted to 0.127 *M* and to 0.0127 *M*.

The protons responsible for the signal at τ −6.78 in the enol triketone, XI, exchanged rapidly with deuterium oxide. In this experiment, 0.1 ml of D_2O was added to a solution of 697 mg of the monoenol triketone, XI, in 2 ml of $CDCl_3$; the spectrum was examined immediately, after 50 min, and after 22 hr.

The protons responsible for the signal at τ 4.90, and for signals at 7.83 and 8.20 did not exchange with deuterium oxide under the conditions given above.

Base Catalysis of the Equilibration of the Dienol Diketone, XII, with the Monoenol Triketone, XI, in $CDCl_3$ Solution.—A solution of the dienol diketone, XII (mp 154°), in $CDCl_3$ was treated with two drops of triethylamine. The H^1 nmr spectrum was examined after 20 min and was found to consist of a broad signal at τ −6.7, a sharp signal at 4.90, two sharp signals at 7.83 and 8.20, and a sharp signal at 8.13; the latter had the same integrated intensity as the sum of the other two. A solution of the monoenol triketone, XI (mp 114°), in $CDCl_3$ was treated with a few drops of triethylamine. The H^1 nmr spectrum was examined after 5 min and was found to be identical with the spectrum described above, indicating rapid equilibration between the two tautomeric forms in solution in the presence of an amine. No further change was noted in a spectrum taken after 2 hr.

Reaction of the Dienol Diketone, XII, with Hydrazine. Formation of a Bispyrazole, XIII.—Hydrazine hydrate (2.0 ml of 64% aqueous solution) was added to a solution of the dienol diketone, XII (1.0 g), in ethanol (35 ml), and the mixture was kept 1.5 hr at reflux. The crystals which separated (830 mg, 86%) were recrystallized from boiling ethanol (60 ml), giving 1,2-bis-4′-(3′,5′-dimethyl)pyrazolylbenzene, XIII, which did not melt below 350°.

Anal. Calcd for $C_{16}H_{18}N_4$: N, 21.1. Found: N, 21.2.

The bispyrazole, XIII, was insoluble in methylene chloride, ethyl acetate, dimethylformamide, and nitromethane. The infrared spectrum of the solid in a Nujol mull had no band in the carbonyl region 5.5 to 6.2 μ; it had bands at 3.2, 6.32, 7.70, 7.85, 8.10, 8.70, 9.40, 9.95, 11.70, 12.5, 12.82, and 13.20 μ. The H^1 nmr spectrum in $AsCl_3$ had signals at τ −3.78 (NH), 2.6 (aromatic), and 7.90 (methyls) in the proportion of 2:4:12.

Reaction of the Monoenol Triketone, XI, with Hydrazine. Formation of the Bispyrazole, XIII.—Hydrazine hydrate (1.0 ml of 64% aqueous solution) was added to a solution of the crystalline monoenol triketone, XI, (300 mg, mp 114°) in ethanol (20 ml). The mixture was kept 1 hr at reflux, and the crystals that separated were filtered. This material (240 mg, 90%) did not melt below 350°; the infrared spectrum of the solid in a Nujol mull and the H^1 nmr in $AsCl_3$ were identical with that of the bispyrazole, XIII, prepared from XII.

Preparation of a Diastereomer of 1-Phenyl-2-acetylpropylene Oxide.[9]—Benzaldehyde (11.9 g) was added to a solution of 3-chloro-2-butanone (9.6 g) in methanol (10 ml) at 0°. The solution was treated with a solution of 1.9 g of sodium in 28 ml of methanol. The addition was carried out over a 1-hr period. The solvent was removed, the residue was diluted with H_2O (25 ml), and the solution was treated with 6 N acetic acid (5 ml). Extraction with ether and distillation of the ether solution through a 6-in. Vigreaux column gave the keto epoxide, VI, bp 107–108° (3.0 mm), yield 6.5 g (40%). The infrared spectrum had bands at 5.95 (s), 7.40 (m), and 8.80 (m) μ (CH_2Cl_2). The H^1 nmr spectrum (pure liquid) had a 5 H^1 signal at τ 2.73, a 1 H^1 signal at 5.73, a 3 H^1 signal at 7.90, and a 3 H^1 signal at 8.80.

Attempts at Rearrangement of 1-Phenyl-2-acetylpropylene Oxide. A. In Pure Methanol.—The epoxide (1.8 g) in methanol (12 ml) was refluxed for 6 hr. The methanol was removed and the residue was shown to contain the unchanged epoxide, VI, by H^1 nmr spectrometry.

B. In Methanol Containing One Mole of Trimethyl Phosphate.—The epoxide, VI, remained unchanged after 1 hr at reflux temperature.

C. In Methanol Containing Phosphoric Acid.—A 1 M solution of the epoxide in methanol was treated with 23 mole % of H_3PO_4. The mixture was refluxed for 24 hr. The methanol was removed at 20° (1 mm). The residue was treated with H_2O, and extracted with ether. Distillation of the ether left a colorless oil whose H^1 nmr (pure liquid) had signals due to the unreacted epoxide, VI (τ 2.72, 5.73, 7.90, and 8.82), and the dienol diketone, XII (τ 8.20). Integration of these signals indicated the formation of approximately 23% of the dienol diketone, XII.

Reaction of One Mole of the Biacetyl–Trimethyl Phosphite Adduct, I, with One Mole of Terephthalaldehyde.—A solution of the biacetyl–trimethyl phosphite adduct, I (22.4 g, 106.7 mmoles), in 50 ml of methylene chloride was slowly added to a solution of terephthalaldehyde (14.3 g, 106.7 mmoles) in 50 ml of methylene chloride at 0°. The addition required 30 min and the reaction was slightly exothermic. The solution was kept at 20° for 24 hr. The solvent was removed and the thick colorless oil was dissolved in 50 ml of ether. The solution was kept first at 20° and then at 0° for several days until crystallization occurred; the crystals were collected and dried at 20° (0.5 mm). 2,2,2-Trimethoxy-4β-methyl-4α-acetyl-5-*p*-formylphenyl-1,3,2-dioxaphospholane, XIVa (22 g, 60%), had mp 74–78°.

Anal. Calcd for $C_{15}H_{21}O_7P$: P, 9.0. Found: P, 9.0.

The infrared spectrum (CCl_4) had bands at 5.80 and 5.85 μ. The H^1 nmr spectrum ($CDCl_3$) had a singlet at τ 0.00 (aldehyde protons), a multiplet at 2.5 (aromatic protons), a doublet (J_{HP} = 4.5 cps) at 5.23 (protons on phospholane ring), a singlet at 8.10 (acetyl *cis* to phenyl), and a singlet at 8.32 (methyl *cis* to H); δ P^{31} (CH_2Cl_2) +51.2 ppm.

The H^1 nmr of the original reaction mixture showed the presence of relatively small amounts of the diastereomer with *trans*-CH_3/H, XIVb.

Reaction of Two Moles of the Biacetyl–Trimethyl Phosphite Adduct, I, with One Mole of Terephthalaldehyde.—A suspension of terephthalaldehyde (17.2 g, 128.3 mmoles) in methylene chloride (25 ml) was treated with the biacetyl–trimethyl phosphite adduct, I, (67.3, 320 mmoles) at 20° under N_2. The exothermic reaction brought the solution to reflux. The clear solution was cooled to 0° after 10 min and the mixture became solid. It was diluted with 25 ml of methylene chloride and kept at 20° for 24 hr. An aliquot of the solid was analyzed by H^1 nmr spectrometry in $CDCl_3$ solution; the mixture consisted mostly of the isomer XVa with a *cis*-CH_3/H, *cis*-CH_3/H configuration (vide infra). There were indications of the presence of a second isomer with poorly resolved signals at τ 8.17, and 8.28, possibly the *cis,trans* isomer, XVb.

The above mixture of isomers was treated with boiling benzene (300 ml) and the resulting clear solution was kept at 10° for 5 hr. The pure *cis,cis* isomer, XVa, (30 g, 42%) was recrystallized from benzene, giving the analytical sample of XVa with mp 154–155°.

Anal. Calcd for $C_{22}H_{36}O_{12}P_2$: C, 47.6; H, 6.5; P, 11.2. Found: C, 47.3; H, 6.6; P, 11.1.

The infrared spectrum had strong bands at 5.80 and 9.2–9.4 μ (CH_2Cl_2).

The H^1 nmr spectrum ($CDCl_3$) had a 4 H^1 signal at τ 2.7 (aromatic), a 2 H^1 doublet (J_{HP} = 4.0 cps) at 5.32 (equivalent hydrogens on the phospholane ring), an 18 H^1 doublet (J_{HP} = 12.8 cps) at 6.30 (six equivalent or indistinguishable methoxy groups on phosphorus), a 6 H^1 singlet at 8.30 (two equivalent acetyls), and a 6 H^1 singlet at 8.40 (two equivalent methyls); δ P^{31} +51.1 ($CDCl_3$).

Methanolysis of the *cis,cis*-CH_3/H of the Bisphospholane Made from Two Moles of the Biacetyl–Trimethyl Phosphite Adduct, I, and One Mole of Terephthalaldehyde.—The crystalline *cis,cis* isomer, XVa (21 g), was suspended in methanol (75 ml) and the mixture was heated to reflux; the clear solution became turbid after 2 hr and was then cooled to 20°. Crystals of the dienol diketo form, XVII, of 1,4-bis(diacetylmethyl)benzene separated out. This material had mp 180–190° (5.3 g, 51%). One recrystallization from benzene gave the analytical sample of the pure tautomer, XVII, with mp 191–192°.

Anal. Calcd for $C_{16}H_{18}O_4$: H, 70.1; H, 6.5. Found: C, 70.1; H, 6.5.

The infrared spectrum (CH_2Cl_2) had a strong broad band centered at 6.25 μ, and bands at 7.20 and 7.60 μ.

The H^1 nmr spectrum ($CDCl_3$) had a 2 H^1 singlet at τ −6.60, (enol OH), a 4 H^1 signal at 2.8 (aromatic), and a 12 H^1 singlet at 8.08.

The mother liquid from the isolation of the tautomer, XVII, gave additional XVII after crystallization (*ca.* 1.5 g).

A solution of the dienol diketone, XVII, in $CDCl_3$ was treated with two drops of triethylamine. The H^1 nmr spectrum did not change within 20 min.

Reaction of the Dienol Diketone, XVII, with Hydrazine. Formation of 1,4-Bis-4′-(3′,5′-dimethyl)pyrazolylbenzene.—A solution of the dienol diketone, XVII (1.0 g), in ethanol (50 ml) was treated with 1.5 ml of 64% aqueous solution of hydrazine hydrate. The solid separated immediately. The mixture was heated to reflux for 2 hr, cooled, and filtered. The bispyrazole, XVIII (0.87 g), melted at approximately 418°. It was insoluble in most solvents, but could be recrystallized from boiling dimethylformamide (0.8 g in 50 ml).

Anal. Calcd for $C_{16}H_{18}N_4$: C, 72.2; H, 6.8; N, 21.0. Found: C, 71.5; H, 6.8; N, 22.0.

Registry No.—IIa, 14179-51-2; IIb, 14179-52-3; IIIa, 10591-64-7; IIIb, 11591-65-8; V, 14179-55-6; VI, 14179-56-7; VIII, 6668-24-2; XI, 14181-21-6; XII, 14181-22-7; XIII, 14181-23-8; XIVa, 14181-24-9; XVa, 14271-17-1; XVII, 14181-25-0; XVIII, 14181-26-1; phthaladehyde, 643-79-8; terephthaladehyde, 623-27-8.