# Polypentaoxyphosphoranes. Carbon–Carbon Condensations from the Reaction of Phthalaldehyde with Trimethyl Phosphite and with 1,3,2-Dioxaphospholenes[1,2]

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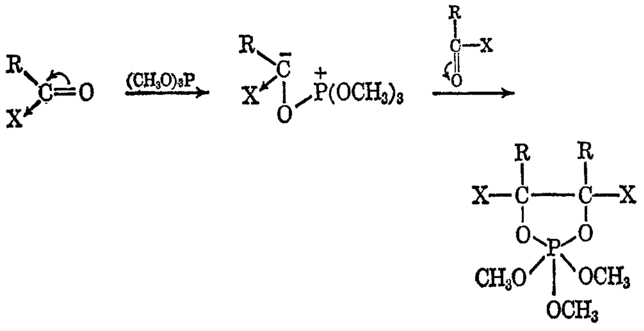
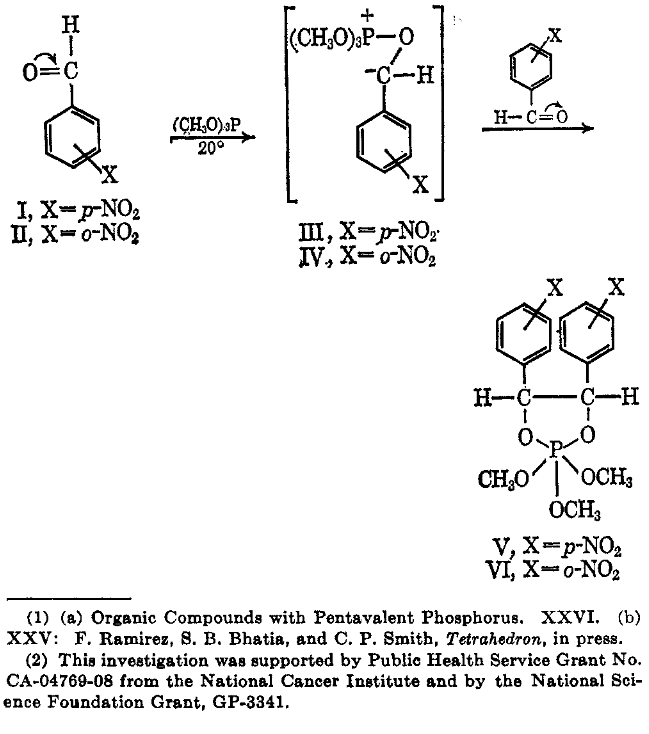
The phosphorus of trimethyl phosphite attacked the oxygen of one of the two carbonyl functions present in phthalaldehyde. The resulting 1:1 adduct condensed with a second molecule of phthaldehyde giving the *meso* and the racemic forms of a 2,2,2-trimethoxy-1,3,2-dioxaphospholane in the proportion 80:20. This monopentaoxyphosphorane had two aldehyde functions which underwent stepwise reaction with 1 and 2 moles of a 2,2,2-trialkoxy-1,3,2-dioxaphospholene (such as the 1:1 adduct made from biacetyl and trimethyl phosphite). The products were bis- and trispentaoxyphosphoranes, formed stereoselectively. The two aldehyde groups in phthalaldehyde underwent stepwise reaction with 1 and 2 moles of the 1,3,2-dioxaphospholene and gave the corresponding mono- and bispentaoxyphosphoranes. The $P^{31}$ and the $H^1$ nmr spectral data are given.

The condensation of two molecules of a carbonyl compound with one molecule of a trialkyl phosphite to yield a 2,2,2-trialkoxy-1,3,2-dioxaphospholane was first reported[3] in 1961. Since then, a number of examples of this reaction have been described.[4] The essential feature is the presence in the molecule of a suitably activated carbonyl function. This activation is necessary in order to provide the stabilization of the negative charge that develops on a carbon when the phosphite adds to the carbonyl oxygen. Thus, trialkyl phosphites do not react with benzaldehyde below 100°; however, they react with *p*- and *o*-nitrobenzaldehydes at 20° or below.[1b]



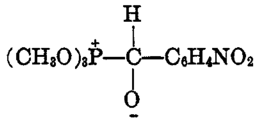


I, X=*p*-$NO_2$
II, X=*o*-$NO_2$

III, X=*p*-$NO_2$
IV, X=*o*-$NO_2$

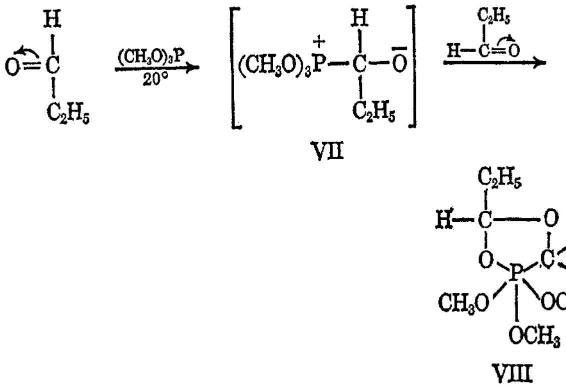
V, X=*p*-$NO_2$
VI, X=*o*-$NO_2$

The formation of the pentaoxyphosphoranes V and VI implies the formation of 1:1 adducts like III and IV, in which there is a new phosphorus–oxygen bond. However, it is entirely possible that the phosphite and nitrobenzaldehydes are involved also in a rapid equilibrium with a 1:1 adduct having a P–C bond.



$$(CH_3O)_3\overset{+}{P}—\overset{H}{\underset{O^-}{C}}—C_6H_4NO_2$$

In fact, this was shown to occur in the case of simple *aliphatic* monoaldehydes,[5] where the final product was a stable 2,2,2-trialkoxy-1,4,2-dioxaphospholane VIII, formed presumably *via* the 1:1 adduct VII. Evidently, the pathway leading to the 1,3,2-dioxaphospholane was not accessible to the unsubstituted aliphatic monoaldehydes.



VII

VIII

This paper is concerned with the behavior of aromatic dialdehydes toward trialkyl phosphites. We have also studied the reaction of the dialdehydes with 2,2,2-trialkoxy-1,3,2-dioxaphospholenes,[4] for example, the 1:1 adduct IX prepared from biacetyl and trimethyl phosphite. This phospholene undergoes nucleophilic addition to benzaldehyde with formation of a phospholane (X).[6]

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[1] (a) Organic Compounds with Pentavalent Phosphorus. XXVI. (b) XXV: F. Ramirez, S. B. Bhatia, and C. P. Smith, *Tetrahedron*, in press.

[2] This investigation was supported by Public Health Service Grant No. CA-04769-08 from the National Cancer Institute and by the National Science Foundation Grant, GP-3341.

[3] (a) F. Ramirez and N. Ramanathan, *J. Org. Chem.*, **26**, 3041 (1961); (b) F. Ramirez, N. Ramanathan, and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 1317 (1962).

[4] For a review with many references, see F. Ramirez, *Bull. Soc. Chim. France*, 2443 (1966).

[5] F. Ramirez, A. V. Patwardhan, and S. R. Heller, *J. Am. Chem. Soc.*, **86**, 514 (1964).

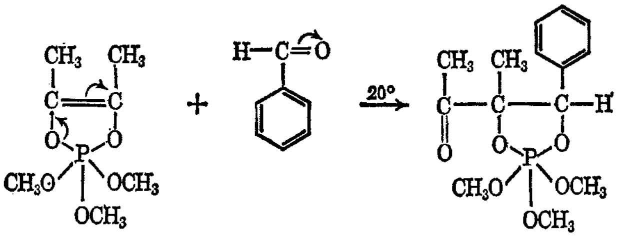
[6] F. Ramirez, A. V. Patwardhan, N. Ramanathan, N. B. Desai, C. V. Greco, and S. R. Heller, *ibid.*, **87**, 543 (1965).

Table I

Nmr Shifts[a] of 2,2,2-Trimethoxy-1,3,2-dioxaphospholanes from the Reaction of *o*-Phthalaldehyde (PA) with Trimethyl Phosphite (TMP) and with the Biacetyl Trimethyl Phosphite 1:1 Adduct[b] (BI-TMP)

| Compn of dioxaphospholane | No. | δ ($P^{31}$) | τ (Ac)[c] | τ (Me)[c] | τ (H)[d] | $J_{HP}$[d] | τ (H)[e] | $J_{HP}$[e] | τ (HCO)[f] | τ (MeO)[g] | $J_{HP}$[g] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2PA-TMP | XIIa | +49.9 | None | None | 3.60 | 11.5 | None | None | 0.13 | 6.22 | 12.6 |
| | XIIb | +50.1 | None | None | 4.32 | 3.5 | None | None | 0.40 | 6.24 | 12.6 |
| 2PA-BI-2TMP | XVa | +50.1 | 8.30 | 8.48 | 3.7–4.3 | ... | 5.15 | 7.5 | 0.14 | 6.15, 6.32 | 13.0, 13.0 |
| | XVb | ... | 7.60 | 9.20 | | ... | ... | ... | 0.10 | ... | ... |
| 2PA-2BI-3TMP | XVIa | +49.9 | 8.28, 8.29 | 8.41, 8.53 | 3.8–4.5 | ... | 4.90, 5.15 | 9.0, 3.0 | None | 6.25, 6.26, 6.42 | 12.5, 12.5, 12.5 |
| | XVIb | ... | 7.62 | 9.20 | | ... | ... | ... | None | ... | ... |
| PA-BI-TMP | XVIIa | +49.6 | 8.30 | 8.45 | None | None | 4.05 | 9.5 | −0.12 | 6.32 | 12.7 |
| | XVIIb | +51.1 | 7.60 | 9.20 | None | None | 3.83 | 5.2 | 0.00 | 6.33 | 12.7 |
| PA-2BI-2TMP | XVIIIa | +49.3 | 8.28 | 8.32 | None | None | 4.83 | 10.0 | None | 6.32 | 12.8 |
| | XVIIIb | +49.5 | 8.22, 7.60 | 8.25, 9.15 | None | None | 4.10, 4.75 | 18.0, 9.5 | None | 6.38, 6.40 | 12.8, 12.8 |
| | XVIIIc | ... | 7.58 | 9.09 | None | None | ... | ... | None | 6.40 | 12.8 |
| 2ONB[h]-TMP | VIa | +50.1 | None | None | 3.83 | 11.5 | None | None | None | 6.25 | 12.8 |
| | VIb | ... | None | None | 4.55 | 5.2 | None | None | None | 6.30 | 12.8 |
| 2PNB[i]-TMP | Va | +49.6 | None | None | 4.60 | 11.8 | None | None | None | 6.25 | 12.6 |
| | Vb | +50.2 | None | None | 5.30 | 2.2 | None | None | None | 6.28 | 12.8 |
| B[j]-BI-TMP | Xa | +51.5 | 8.40 | 8.52 | None | None | 5.45 | 5.6 | None | 6.42 | 12.5 |
| | Xb | ... | 7.76 | 9.18 | None | None | ... | ... | None | 6.45 | 12.6 |

[a] δ ($P^{31}$) at 40.5 Mcps, in parts per million (ppm) *vs.* $H_3PO_4$, in $CH_2Cl_2$. $H^1$ nmr at 60 Mcps, in ppm *vs.* tetramethylsilane = 10, τ values in $CDCl_3$. $J_{HP}$ = coupling in cycles per second (cps). [b] 2,2,2-Trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene. [c] Acetyl and methyl groups derived from biacetyl. [d] Hydrogen on dioxaphospholane ring bearing two phenyl substituents. [e] Hydrogen on dioxaphospholane ring bearing phenyl, methyl, and acetyl substituents. [f] Hydrogen on aldehyde group. [g] Methoxy group on phosphorus. [h] *o*-Nitrobenzaldehyde. [i] *p*-Nitrobenzaldehyde. [j] Benzaldehyde.

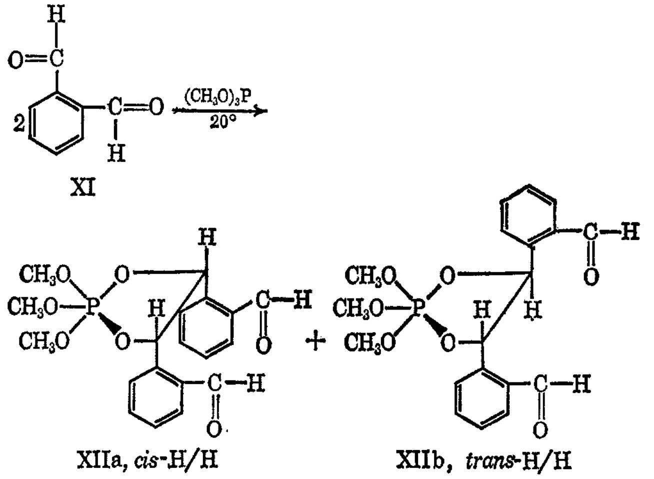


IX

X

## Results

**Reaction of Phthalaldehyde with Trimethyl Phosphite.**—Phthalaldehyde XI reacted with trimethyl phosphite at 20°. Only one of the two aldehyde functions present in the molecule was attacked by the phosphite; the products were the *meso* and the racemic forms of 2,2,2-trimethoxy-4,5-di-*o*-formylphenyl-1,3,2-dioxaphospholane (XIIa and XIIb), which were produced in the approximate proportion 80:20. The isomers were separated by crystallization from benzene–hexane.



XI

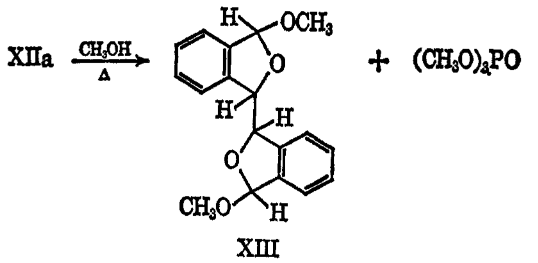
XIIa, *cis*-H/H

XIIb, *trans*-H/H

The structure and the configuration of the products are based on the following data: (1) the presence of strong infrared absorption at 5.93 μ due to the aldehyde groups; (2) the strongly positive value[4] of the $P^{31}$ nmr signals, which are listed in Table I; (3) the presence of a two-proton doublet, a two-proton singlet, and a nine-proton doublet in the $H^1$ nmr spectrum of the major isomer XIIa. The position of these signals and the value of the coupling constants, are given in Table I. The minor isomer XIIb gave rise to a corresponding set of signals. Note that the two equivalent protons in the dioxaphospholane ring of the *minor isomer* XIIb gave a doublet at a significantly *higher* magnetic field than the corresponding protons of the major isomer XIIa; this suggested that the ring protons of the minor isomer were shielded by phenyl rings as in formula[4,6] XIIb. These protons were less effectively coupled with the phosphorus nucleus ($J_{HP}$ = 3.5 cps) than the protons of the major or *meso* isomer XIIa ($J_{HP}$ = 11.5 cps); this would be understandable if the dihedral angle formed by the planes H-C-O and P-O-C was closer to 90° in racemic XIIb than in *meso* XIIa.

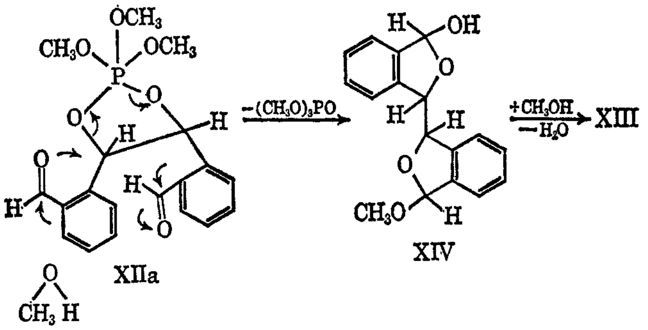
Table I includes, for comparison purposes, the spectral data for the 1,3,2-dioxaphospholanes V and VI made from the nitrobenzaldehydes.[1b]

The establishment of a carbon–carbon bond in the phthalaldehyde–trimethyl phosphite 2:1 adduct XII was demonstrated also by chemical means. The adduct XIIa lost a molecule of trimethyl phosphate when heated in methanol solution; the other product of this reaction is formulated as bis-3-methoxyphthalanyl (XIII) from the data given in the Experimental Section.

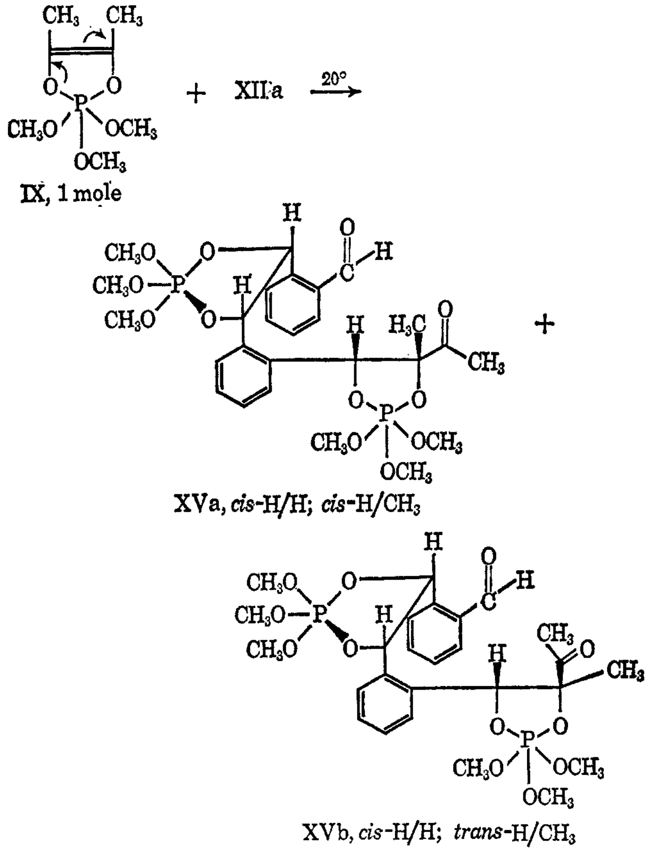


XIII

A possible course of the reaction is shown below and involves as intermediate the cyclic acetal–hemiacetal XIV derived from hydrobenzoin-*o*-dialdehyde.[7]



**Reaction of Aldehyde-Containing 2,2,2-Trialkoxy-1,3,2-dioxaphospholanes with 2,2,2-Trialkoxy-1,3,2-dioxaphospholenes.**—The reaction of 1 mole of 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (IX) with 1 mole of the pure *meso* isomer XIIa made from phthalaldehyde and trimethyl phosphite, gave the two diastereomeric forms XVa and XVb of a bispentaoxyphosphorane in the approximate XVa:XVb proportion 65:35.



The infrared spectrum of the bispentaoxyphosphoranes had two carbonyl bands. The P$^{31}$ nmr shift of the major isomer XVa is given in Table I; it was not possible to resolve the signals owing to the two phosphorus nuclei present in the same molecule.

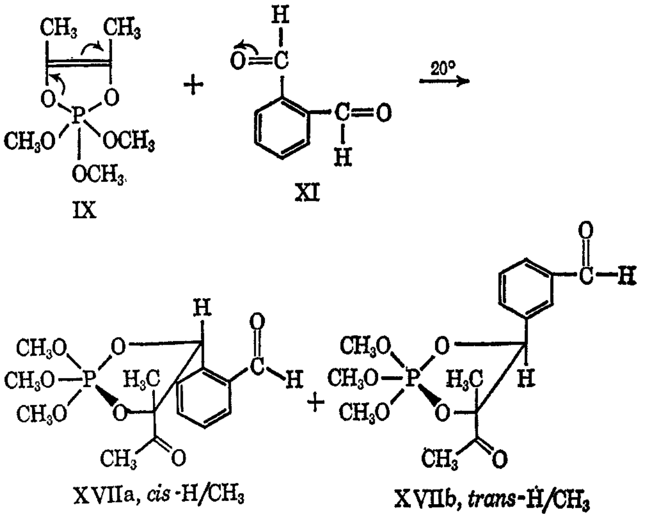
The H$^1$ nmr signals of XVa and XVb are listed in Table I. Note for comparison the corresponding signals of the monopentaoxyphosphorane X made from the reaction of the phospholene IX with benzaldehyde.[6] In the *cis,cis* isomer XVa the acetyl group is next to a phenyl ring; hence the H$^1$ nmr signal for the acetyl protons should be shifted to high magnetic field relative to that of the *cis,trans* isomer XVb (*cf.* $\tau$ 8.30 *vs.* 7.60). The opposite should be the case for the signals due to the methyl groups attached to the phospholane ring (*cf.* $\tau$ 8.48 *vs.* 9.20).[4]

When an excess of the phospholene IX was treated with the *meso* isomer XIIa, the two aldehyde functions engaged in carbon–carbon condensations. Three diastereomeric trispentaoxyphosphoranes, XVIa, XVIb, and XVIc, can be formed in this reaction (Scheme I); however, only one of them was obtained in crystalline state. This must have the *cis,cis,trans* configuration (XVIa), since the H$^1$ nmr spectrum had signals due to *two* nonequivalent acetyl groups and *two* nonequivalent methyl groups. The other isomers, *cis,cis,cis* XVIc and *cis,trans,trans* XVIb, should give one signal for the two equivalent acetyls and one signal for the two equivalent methyl groups. Examination of the crude mixture of isomers formed in the reaction showed the presence of small amounts of a second isomer thought to have the *cis,trans,trans* configuration (XVIb) from the H$^1$ nmr data in Table I.

The identical *cis,cis,trans*-trispentaoxyphosphorane (XVIa) was made from the reaction of 1 mole of the phospholene IX with 1 mole of the pure *cis,cis*-bispentaoxyphosphorane (XVa).

It was possible to convert phthalaldehyde XI into the trispentaoxyphosphorane XVIa directly, without isolation of intermediates.

**Reaction of Phthalaldehyde with 2,2,2-Trialkoxy-1,3,2-dioxaphospholenes.**—The first aldehyde group of phthalaldehyde condensed readily with one molecule of the dioxaphospholene IX. The products were the *cis* and the *trans* forms of a pentaoxyphosphorane XVIIa and XVIIb, formed in the proportion 60:40.



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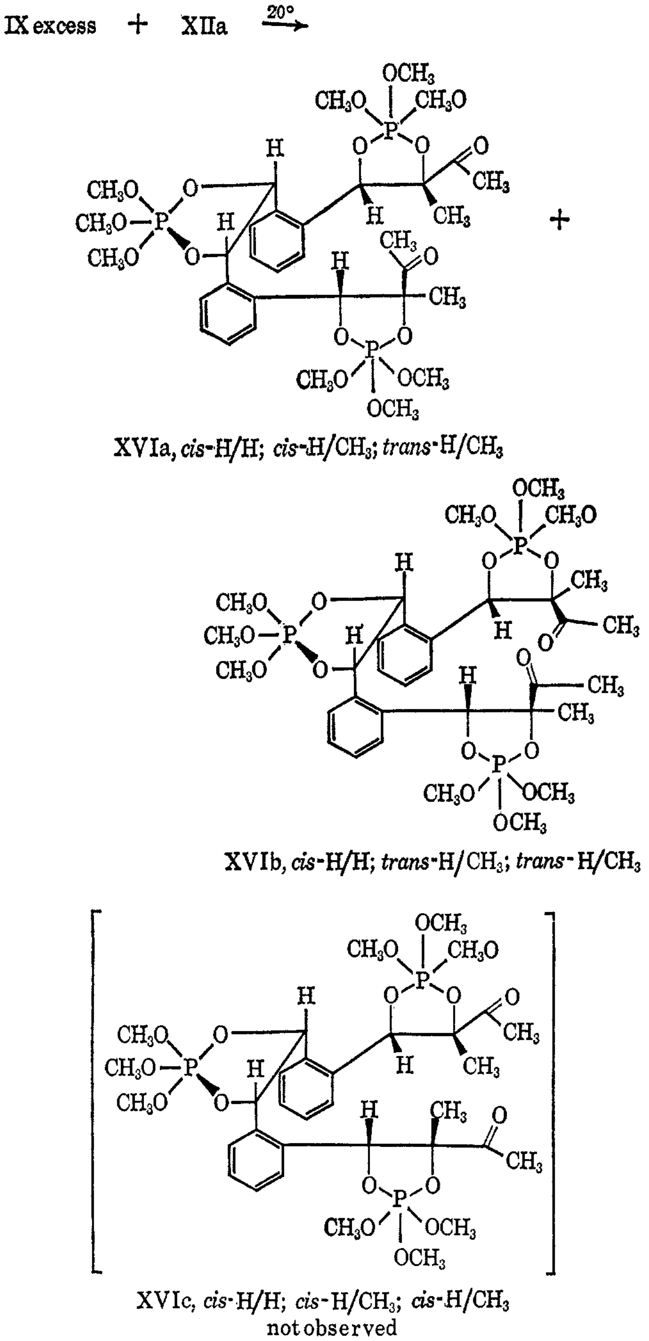
[7] The reductive dimerization of phthalaldehyde by means of zinc and acetic acid was reported by J. Thile and E. Weitz, *Ann.*, **377**, 1 (1910).

SCHEME I

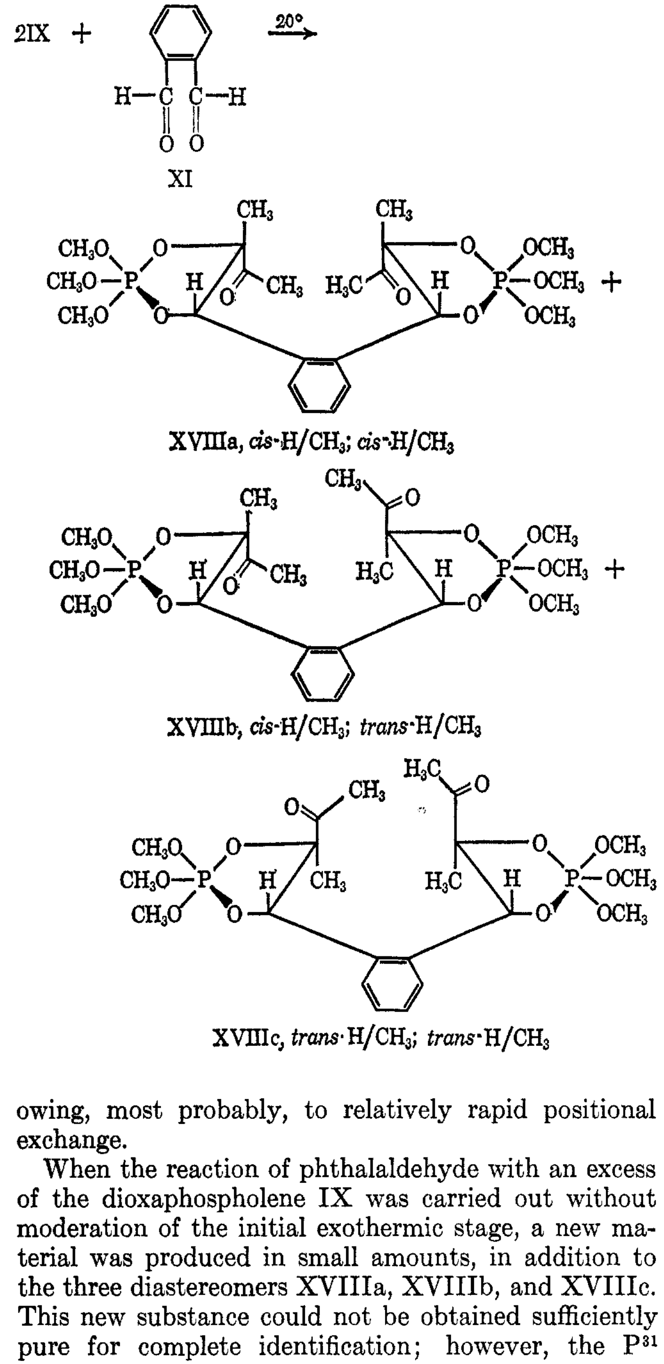


XVIa, *cis*-H/H; *cis*-H/$CH_3$; *trans*-H/$CH_3$

XVIb, *cis*-H/H; *trans*-H/$CH_3$; *trans*-H/$CH_3$

XVIc, *cis*-H/H; *cis*-H/$CH_3$; *cis*-H/$CH_3$
not observed

SCHEME II



XVIIIa, *cis*-H/$CH_3$; *cis*-H/$CH_3$

XVIIIb, *cis*-H/$CH_3$; *trans*-H/$CH_3$

XVIIIc, *trans*-H/$CH_3$; *trans*-H/$CH_3$

The nmr data are given in Table I. The configurations are assigned on the basis of the arguments discussed above.

The two aldehyde functions of phthalaldehyde could be condensed with the dioxaphospholene IX. The three expected diastereomers of the bispentaoxyphosphorane were formed in the approximate proportion 30:60:10 for XVIIIa:XVIIIb:XVIIIc (Scheme II).

The major isomer must have the *cis,trans* configuration XVIIIb since its $H^1$ nmr spectrum had two signals due to the nonequivalent acetyl groups, two signals due to the nonequivalent methyl groups, two doublets due to the nonequivalent protons on the two dioxaphospholane rings, and two doublets due to the two sets of three methoxy groups. The couplings are due to the $P^{31}$–$H^1$ spin–spin coupling. As in previous cases,[4] the three methoxy groups attached to quintuply connected phosphorus could not be resolved at 20°, owing, most probably, to relatively rapid positional exchange.

When the reaction of phthalaldehyde with an excess of the dioxaphospholene IX was carried out without moderation of the initial exothermic stage, a new material was produced in small amounts, in addition to the three diastereomers XVIIIa, XVIIIb, and XVIIIc. This new substance could not be obtained sufficiently pure for complete identification; however, the $P^{31}$ nmr shift was strongly positive suggesting a pentaoxyphosphorane structure. These and other reactions of the new polypentaoxyphosphoranes will be described elsewhere.

## Discussion

The reaction of phthalaldehyde with trialkyl phosphites provides another example of attack by phosphorus on carbonyl oxygen in a system in which the carbonyl function is activated by electron-withdrawing groups.[4] Furthermore, this paper provides information on the relative reactivity of two carbonyl functions present in the same molecule toward trialkyl phosphites and toward the dioxaphospholenes. This information is valuable in polymerization reactions by means of the new *oxyphosphorane carbon–carbon condensation.* This type of polymerization is under investigation now in this laboratory.

## Experimental Section

The analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The instrumentation was described previously.[4] The following abbreviations are used: PA = phthalaldehyde, BI = biacetyl, TMP = trimethyl phosphite.

**Reaction of PA with TMP. Formation of the *cis*-H/H and *trans*-H/H Isomers of a Dioxaphospholane with the Composition 2PA-TMP (XIIa and XIIb).**—The trimethyl phosphite was dried over sodium ribbon and distilled with protection against moisture. The phthalaldehyde was freshly crystallized from hexane. The phosphite (16.7 g, 137 mmoles) and the dialdehyde (9.2 g, 68 mmoles) were mixed and kept at 20°, under $N_2$, with stirring. An exothermic reaction was noted within 20 min, and crystals separated thereafter. Benzene (25 ml) was added after 24 hr, and the crystals (9.2 g, 70%, mp 105–106°) were filtered. One crystallization from benzene–hexane gave *meso*-2,2,2-trimethoxy-4,5-di-*o*-formylphenyl-1,3,2-dioxaphospholane (XIIa, 7.0 g, 55%), mp 114–122°; a second crystallization gave the analytical sample of XIIa (5.0 g, 40%) melting at 123–124°.

*Anal.* Calcd for $C_{19}H_{21}O_7P$: C, 58.2; H, 5.4; P, 7.9. Found: C, 57.9; H, 5.5; P, 7.7.

The H$^1$ and P$^{31}$ nmr signals are given in Table I. The infrared spectrum (in $CCl_4$) had bands at 5.93 (vs, C=O), 6.26 (w), 6.37 (w), 6.90 (w), 8.33 (m), 8.44 (m), 9.22 (vs), and 9.42 (vs, $POCH_3$), and 9.61 $\mu$ (shoulder).

The benzene–hexane mother liquids from which 40% of pure *meso* XIIa had been removed were collected and concentrated to a small volume, yielding 3.2 g (25%) of additional pure *meso* XIIa, mp 123–124° (total yield 65%). No attempt was made to purify the racemic form, which could not be obtained in crystalline state; its nmr signals are given in Table I. The formation of some trimethyl phosphate in this reaction was demonstrated by examination of the P$^{31}$ and the H$^1$ nmr spectra of the residue. Formation of phosphate seemed to be favored by relatively high temperatures during the reaction.

In another experiment, in which phthalaldehyde was stirred with 3 mole equiv of trimethyl phosphite for 20 hr at 20°, it was shown by H$^1$ nmr spectroscopy that the crude product consisted of a mixture of the *meso* XIIa and racemic XIIb isomers in the approximate proportion 80:20, respectively. The reaction was carried out also in benzene and in methylene chloride solutions at 20°; in these cases, the reaction was complete in about 3 days, and there was little trimethyl phosphate formed as a by-product.

**Reaction of the *meso*-PA-TMP 2:1 Adduct (XIIa) with Methanol.**—A suspension of the dioxaphospholane XIIa (1.0 g) in methanol (40 ml) was stirred at 20°. A clear solution was obtained in 2 hr. Most of the methanol was removed (20°, 20 mm) after 24 hr. The first crop of the phosphorus-free product (380 mg) had mp 160–185°; a second crop (90 mg, mp 160–180°) was obtained by dilution of the filtrate with water; the yield of XIII was 60%. One crystallization from benzene–hexane gave **3,3′-dimethoxy-1,1′-bis(1,3-dihydroisobenzofuranyl)** or **bis-3-methoxyphthalanyl (XIII)**, mp 204–205°.

*Anal.* Calcd for $C_{18}H_{18}O_4$: C, 72.5; H, 6.0; mol wt, 298. Found: C, 72.6; H, 6.3; mol wt, 308.

The H$^1$ nmr spectrum (in $CDCl_3$) had an 8 H$^1$ multiplet at $\tau$ 2.6 (aromatic), a 2 H$^1$ singlet at 4.40 (acetal protons), a 2 H$^1$ singlet at 5.10 (ether protons), and a 6 H$^1$ singlet at 6.35 ($CH_3O$ protons). The infrared spectrum (in $CH_2Cl_2$) had no bands in the carbonyl region (4.0 to 6.2 $\mu$); it had bands at 6.71 (w), 6.85 (w), 7.27 (m), 7.41 (m), 8.30 (m), 8.44 (m), 9.17 (s), 9.57 (s), 9.76 (s), 10.0 (mw), 10.3 (mw), 10.6 (mw), and 10.7 $\mu$ (mw).

**Reaction of 1 Mole of the BI-TMP 1:1 Adduct (IX) with 1 Mole of the *meso*-PA-TMP 2:1 Adduct (XIIa). Formation of the *cis*-H/H-*cis*-H/CH$_3$ and the *cis*-H/H-*trans*-H/CH$_3$ Isomers of a Bisdioxaphospholane with Composition 2PA-BI-2TMP (XVa and XVb).**—The dioxaphospholene IX (6.1 g, 28.8 mmoles) was added to a solution of the crystalline *meso*-dioxaphospholane XII (11.3 g, 28.8 mmoles, freshly crystallized) in methylene chloride (25 ml) at 20°, under $N_2$. The solution was stirred at 20° for 4 days, and the solvent was removed at 20° (20 mm). The H$^1$ nmr spectrum of the crude product (in $CDCl_3$) exhibited the signals due to the two diastereomers XVa and XVb of a **bisdioxaphospholane**, in *ca.* 65:35 proportion (*cf.* Table I); in addition, there were signals attributable to one isomer of a **trisdioxaphospholane** (*vide infra*). The crude product was kept for 20 hr at 10° in benzene–hexane (30 + 20 ml). The crystals that separated (6.9 g, 40%, mp 127–135°) proved to be the nearly pure diastereomer ***cis*-H/H-*cis*-H/CH$_3$-2,2,2-trimethoxy-5-*o*-formylphenyl-4-*o*-[5′-(2′,2′,2′-trimethoxy-4′-methyl-4′-acetyl)-1′,3′,2′-dioxaphospholanyl]phenyl-1,3,2-dioxaphospholane (XVa)**, contaminated with some of the *cis*-H/H-*trans*-H/CH$_3$ isomer XVb. One crystallization from benzene–hexane gave the pure *cis,cis* isomer XVa, mp 139–140°.

*Anal.* Calcd for $C_{26}H_{36}O_{12}P_2$: C, 51.8; H, 6.0; P, 10.3. Found: C, 51.6; H, 5.9; P, 10.2.

The H$^1$ and the P$^{21}$ nmr signals are listed in Table I. The infrared spectrum (in $CCl_4$) had strong bands at 5.80 (acetyl C=O), 5.90 (aromatic C=O), 9.20, 9.40, and 9.60 $\mu$ (shoulder, $POCH_3$).

The original mother liquid, from which 40% of the *cis,cis* isomer had been removed, was evaporated. The residue was shown to contain more *cis,cis* isomer XVa and the *cis,trans* isomer XVb (by H$^1$ nmr spectroscopy). In addition, there were the signals due to the trisdioxaphospholane described below.

**Reaction of an Excess of the BI-TMP 1:1 Adduct (IX) with 1 Mole of the *meso*-PA-TMP 2:1 Adduct (XIIa). Formation of the *cis*-H/H-*cis*-H/CH$_3$-*trans*-H/CH$_3$ Isomer XVIa of a Trisdioxaphospholane with Composition 2PA-2BI-3TMP.**—A suspension of the *cis*-H/H isomer of the PA-TMP adduct (11.2 g, 24.3 mmoles) in an excess of the dioxaphospholene IX (30.8 g, 146.5 mmoles) was stirred at 20° under $N_2$. A clear solution was formed within 4 hr; the excess of phospholene IX was removed after 20 hr (bath at 80°, 0.05 mm). The H$^1$ nmr spectrum of the noncrystalline residue in $CDCl_3$ exhibited the signals due to the *cis*-H/H-*cis*-H/CH$_3$-*trans*-H/CH$_3$ isomer of the trisdioxaphospholane XVIa (*vide infra*); relatively weak signals attributable to the *cis,trans,trans* isomer XVIb were also present. An additional signal at $\tau$ 8.18 could be due to some residual phospholene IX.

The crude product was dissolved in 50 ml of ether and the solution was kept for 2 days at −20° to achieve crystallization. The crystals thus obtained were dried at 20° (0.5 mm) yielding 15 g, (62%); this treatment did not remove the ether completely, as shown by the H$^1$ nmr in $CDCl_3$ solution. One more crystallization from ether gave analytically pure *cis*-H/H-*cis*-H/CH$_3$-*trans*-H/CH$_3$-2,2,2-trimethoxy-4,5-bis-*o*-[5′-(2′,2′,2′-trimethoxy-4′-methyl-4′-acetyl)-1′,3′,2′-dioxaphospholanyl]phenyl-1,3,2-dioxaphospholane (XVIa). When this material was dried at 20° (0.5 mm), it was obtained as white crystals softening at 45° and melting at 54–56°, with gas evolution; the H$^1$ nmr spectrum (in $CDCl_3$) disclosed the presence of diethyl ether in the crystals. When these crystals were dried at 56° (0.5 mm), they lost the ether and were converted into a colorless glass.

*Anal.* Calcd for $C_{33}H_{51}O_{17}P_3$: C, 48.8; H, 6.3; P, 11.5. Found: C, 48.2; H, 6.0; P, 11.3.

The spectral characteristics of the crystalline ether solvate and of the noncrystalline, ether-free material were identical, except for the signals due to diethyl ether. The infrared spectrum (in $CH_2Cl_2$) had bands at 5.82 (C=O), 6.90, 7.40, 7.80, 8.50, and 9.2–9.4 $\mu$ ($POCH_3$). The H$^1$ nmr spectrum in $CDCl_3$ solution had two signals separated by 12.5 cps and centered at $\tau$ 6.24; it could be shown that these signals consisted of two unresolved doublets, each one of them due to three equivalent methoxy groups attached to phosphorus. A third doublet, $J_{HP}$ = 12.5 cps, due to the remaining three methoxy groups in the structure, appeared at $\tau$ 6.41. In benzene solution, the three doublets were well resolved, at $\tau$ 6.18, 6.28, and 6.35, respectively. The spectrum in $CDCl_3$ showed also three additional signals, one of these, at $\tau$ 8.28, was twice as intense as the other two, at 8.41 and 8.53, which had the same intensities. In $CH_2Cl_2$ solution, the four singlets expected from structure XVIA were clearly seen at $\tau$ 8.22, 8.34, 8.47, and 8.53. In dilute benzene, the four signals were seen at $\tau$ 8.18, 8.32, 8.59, and 8.62; in more concentrated benzene solution the latter two signals overlapped; $\delta P^{31}$ = +49.9 ppm (in $CH_2Cl_2$); the three phosphorus nuclei could not be differentiated.

Prolonged heating of the trisdioxaphospholane XVIa at 80° or short exposure to higher temperatures resulted in some decomposition and the appearance of a new signal at $\tau$ 8.18 in the H$^1$ nmr spectrum ($CDCl_3$).

**Reaction of 1 Mole of the BI-TMP 1:1 Adduct (IX) with 1 Mole of the *cis*-H/H-*cis*-H/CH$_3$ (2PA-BI-2TMP) Adduct (XVA). Formation of *cis*-H/H-*cis*-H/CH$_3$-*trans*-H/CH$_3$-Trisdioxaphospholane XVIa.**—The phospholene IX (1.1 g, 5.2 mmoles) was added to a solution of the crystalline *cis*-H/H-*cis*-H/CH$_3$ isomer XVa of the bisdioxaphospholane (3.2 g, 5.2 mmoles) in methylene chloride (10 ml). The solution was stirred at 20° for 7 days. The solvent was removed at 20° (20 mm, last traces at 0.3 mm). The $H^1$ nmr spectrum of the residue (in $CDCl_3$) had the signals at $\tau$ 8.30, 8.40, and 8.55 due to the *cis,cis-trans*-trisdioxaphospholane XVIa. The residue was crystallized from ether (20 ml, −20°) and yielded pure XVIa (1.5 g) identified by its physical and spectral properties.

**Direct Condensation of PA, BI, and TMP to the Trisdioxaphospholane XVIa without Isolation of Intermediates.**—A mixture of phthalaldehyde (7.5 g, 56 mmoles) and trimethyl phosphite (27.8 g, 224 mmoles) was stirred at 0° for 4 hr, and at 20° for 20 hr. The excess phosphite was removed first at 20° (0.3 mm), and then at 55° (0.3 mm). The solid residue (12 g) which contained the *cis*- (XIIa) and *trans*- (XIIb) dioxaphospholanes was mixed with the dioxaphospholene IX (14.1 g, 67 mmoles) made from biacetyl and trimethyl phosphite; the mixture was stirred at 20° for 3 days. To obtain crystalline trisdioxaphospholane XVIa, the reaction mixture was stirred with ether (20 ml) first at 20° and then at −20°. The crystals (10.3 g) were filtered after several days; the $H^1$ nmr ($CDCl_3$) had the signals attributed to the *cis,cis,trans*-trisdioxaphospholane XVIa ($\tau$ 8.28, 8.40, and 8.55) and a signal at $\tau$ 8.17 due, possibly, to phospholene IX. One recrystallization from ether (30 ml, −20°) gave the pure trisdioxaphospholane XVIa (6 g, mp 50–60°, as the ether solvate).

**Reaction of 1 Mole of the BI-TMP 1:1 Adduct (IX) with 1 Mole of PA (XI). Formation of the *cis*-H/CH$_3$ and *trans*-H/CH$_3$ Isomers of a Dioxaphospholane with Composition PA-BI-TMP (XVIIa and XVIIb).**—A solution of the dioxaphospholene (10.5 g, 50 mmoles) in methylene chloride (30 ml) was added, dropwise over a 30-min period, to a solution of phthalaldehyde (6.7 g, 50 mmoles) in methylene chloride (30 ml) at 5° under $N_2$. The solvent was removed (20°, 20 mm) after 24 hr at 20°. The $H^1$ nmr spectrum of the residue (in $CDCl_3$) corresponded to that of a mixture of the diastereomeric dioxaphospholanes XVIIa and XVIIb in a 60:40 proportion. This mixture was kept in ether (30 ml) at −20° for 20 hr, at which time crystals had formed. The latter (11.1 g, 65%, mp 58–76°) consisted of the mixture of isomers XVIIa and XVIIb in *ca.* 55:45 proportion. One crystallization from ether (45 ml, at −20°) did not achieve a separation of the isomers; the crystals consisted of a mixture of XVIIa and XVIIb in about 55:45 proportion; its melting point was 70–81°.

*Anal.* Calcd for $C_{15}H_{21}O_7P$: C, 52.3; H, 6.1; P, 9.0. Found: C, 52.6; H, 6.4; P, 8.9.

The $P^{31}$ and $H^1$ nmr signals are listed in Table I. The infrared spectrum (in $CCl_4$) had strong bands at 5.85 (acetyl), and 5.90 (aldehyde), and very strong bands at 9.20 and 9.40 $\mu$ ($POCH_3$).

The original mother liquid, from which 65% of isomers XVIIa and XVIIb had been removed, was kept for 15 days at 0°, and afforded 1.2 g of the same isomer mixture (total yield 72%). The rest of the material could not be obtained crystalline, but had the spectral characteristics of XVIIa and XVIIb.

**Reaction of 2 Moles of the BI-TMP 1:1 Adduct (IX) with 1 Mole of *o*-Phthalaldehyde (XI) in Methylene Chloride Solution. Formation of *cis,cis*-H/CH$_3$, *cis,trans*-H/CH$_3$, and *trans,trans*-H/CH$_3$ Isomers of a Bisdioxaphospholane with Composition PA-2BI-2TMP (XVIIIa, XVIIIb, and XVIIIc).**—A solution of *o*-phthalaldehyde (10.8 g, 80 mmoles) in methylene chloride (70 ml) was added dropwise, over a 30-min period, to a solution of the biacetyltrimethyl phosphite 1:1 adduct IX (33.6 g, 160 mmoles) in methylene chloride (30 ml) at 0°, under $N_2$. The clear solution was kept for 4 days at 20° with stirring. The course of the reaction was followed by $H^1$ nmr spectroscopy; most of the reaction was complete within 48 hr, but some aldehyde remained after 3–4 days. The solvent was removed at 20° (20 mm); the $H^1$ nmr spectrum of the noncrystalline residue (in $CDCl_3$) exhibited the signals due to the three diastereomeric dioxaphospholanes XVIIIa, XVIIIb, and XVIIIc listed in Table I. Ether (40 ml) was added to the crude mixture of isomers and the clear solution was kept for 2 days at −20°. The crystals that separated (fraction 1, 17.2 g, 40%, mp 30–65°) consisted of a mixture of isomers in the approximate proportion of 30:60:10 XVIIIa:XVIIIb:XVIIIc. The filtrate from this crystallization is fraction 2 (*vide infra*). One recrystallization of fraction 1 from ether (70 ml, 5 hr at −20°) gave a crystalline mixture of the *cis,cis* (XVIIIa) and the *cis,trans* (XVIIIb) isomers in about 50:50 proportion; this is fraction 1-1 (5.5 g, mp 38–80°). The filtrate is fraction 1-2 (*vide infra*).

*Anal.* Calcd for fraction 1-1 ($C_{22}H_{36}O_{12}P_2$): C, 47.6; H, 6.5; P, 11.2. Found: C, 47.0; H, 6.5; P, 11.0.

The $H^1$ and $P^{31}$ nmr signals are listed in Table I. The infrared spectrum ($CCl_4$) had a strong band at 5.82 (C=O) and very strong bands at 9.35 and 9.55 $\mu$ ($POCH_3$). Two further crystallizations of fraction 1-1 from benzene–hexane (1:2) gave the pure *cis,cis* isomer XVIIIa, mp 95–100°, with the $H^1$ and $P^{31}$ nmr signals listed in Table I.

**Fraction 1-2.**—The ether filtrate enriched in *cis,trans* isomer XVIIIb, was kept for 9 days at −20°. The crystals that separated (3.7 g, mp 82–90°) proved to be nearly pure *cis,trans* isomer XVIIIb, mp 82–90°, with the nmr signals given in Table I.

The original ether filtrate (fraction 2) from which 40% of a mixture of diastereomers had been removed, was concentrated to a small volume and kept for 2 days at −20°, yielding about 6% of additional crystalline *cis,cis* isomer XVIIIa contaminated with some *cis,trans* isomer XVIIIb. The ether filtrate was evaporated to dryness affording a noncrystalline, nearly colorless residue. The infrared and the $P^{31}$ and $H^1$ nmr spectral characteristics of this material were consistent with those of the pure diastereomers contaminated with approximately 15 to 20% of other substance(s) having the spectral characteristic of phosphate ester(s).

**Reaction of 3 Moles of the Biacetyl Trimethyl Phosphite 1:1 Adduct (IX) with 1 Mole of Phthalaldehyde in the Absence of Solvent.**—A mixture of the phospholene IX (31.5 g, 150 mmoles) and the aldehyde XI (6.7 g, 50 mmoles) was kept at 20° under $N_2$ (no other solvent was employed). An exothermic reaction was noted within 5 min; very little aldehyde remained after 1 hr and none remained after 24 hr. The excess of adduct was removed at 80° (0.11 mm). The residue was kept for 4 hr at −20° under ether, when crystallization occurred. The crystals (12.5 g, 44%) consisted of a mixture of *cis,cis* XVIIIa, *cis,trans* XVIIIb, and *trans,trans* XVIIIc with the former two predominating. In addition, the $H^1$ nmr disclosed two weak singlets at $\tau$ 8.08 and 8.18 which are not due to the isomers XVIIIa–c. The $P^{31}$ nmr signal for this material was at +50.4 ppm; however, the substance has not been obtained in pure state. Its structure and origin are under study.

The crystalline mixture (12.5 g) described above was recrystallized from ether (40 ml, 3 days at −20°) and gave 7 g (23%) of a mixture of *cis,cis* XVIIIa and *cis,trans* XVIIIb in about 40:60 proportion.

**Registry No.**—Xa, 13006-62-7; XIIa, 10591-56-7; XIIb, 10591-57-8; XIII, 10591-58-9; XVa, 10591-59-0; XVb, 10591-60-3; XVIa, 10591-61-4; XVIb, 13016-42-7; XVIIa, 10591-62-5; XVIIb, 10591-63-6; XVIIIa, 10591-64-7; XVIIIb, 10591-65-8; XVIIIc, 10591-66-9; phthaldehyde, 643-79-8; trimethyl phosphite, 121-45-9