

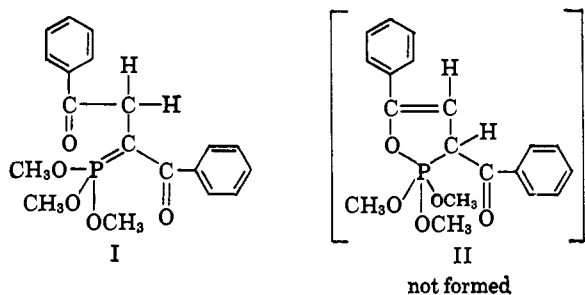
A Crystalline Tetraalkoxyalkylphosphorane from the Reaction of Trimethyl Phosphite with an α,β -Unsaturated Ketone. 3-Benzylidene-2,4-pentanedione. P^{31} and H^1 Nuclear Magnetic Resonance Spectra^{1,2}

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Contribution from the Department of Chemistry of the State University of New York at Stony Brook, Stony Brook, Long Island, New York. Received October 19, 1964

The reaction of trimethyl phosphite with 3-benzylidene-2,4-pentanedione gave a cyclic tetraalkoxyalkylphosphorane, a derivative of the Δ^4 -oxaphospholene ring system with $\delta_{P^{31}} = +27.9$ p.p.m. vs. 85% H_3PO_4 , in the phosphorus n.m.r. spectrum. The crystalline oxyphosphorane was thermally stable and did not react with unsaturated ketones, but was converted into an enol phosphonate by 1 equiv. of water.

A previous paper^{1b} showed that the reaction of *trans*-dibenzoyl ethylene with trimethyl phosphite yielded an alkoxyalkylidenephosphorane (I) rather than a cyclic alkoxyalkylphosphorane (II) as had been previously stated.^{4,5}



This paper deals with the reaction of 3-benzylidene-2,4-pentanedione (III) with trimethyl phosphite, a reaction which gives a crystalline, stable, cyclic tetraalkoxyalkylphosphorane (IV).

Results

When equimolar amounts of 3-benzylidene-2,4-pentanedione (III) and trimethyl phosphite in methylene chloride solution were allowed to react at 20°, a crystalline 1:1 adduct was formed in quantitative

(1) (a) Organic Compounds with Pentavalent Phosphorus, Part XVIII. (b) Part XVII: F. Ramirez and O. P. Madan, Abstracts, Division of Organic Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 13S.

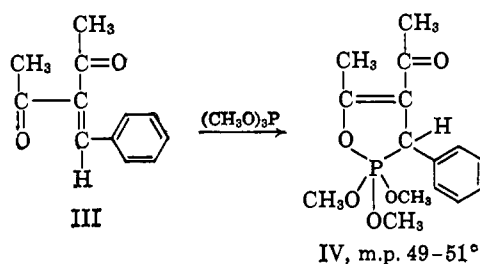
(2) Presented in part in a Plenary Lecture at the IUPAC Symposium on Organophosphorus Compounds, Heidelberg, Germany, May 22, 1964. Preliminary report: F. Ramirez, A. V. Patwardhan, and S. R. Heller, *J. Am. Chem. Soc.*, **86**, 514 (1964).

(3) This investigation was supported by the National Science Foundation (G19509) and by the Public Health Service Research Grant No. CA-04769-05 from the National Cancer Institute.

(4) V. A. Kukhtin and K. M. Orekhova, *J. Gen. Chem. USSR*, **30**, 1539 (1960).

(5) R. G. Harvey and E. V. Jensen, *Tetrahedron Letters*, No. 26, 1801 (1963).

yield. This adduct is formulated as 2,2,2-trimethoxy-3-phenyl-4-acetyl-5-methyl- Δ^4 -oxaphospholene (IV), for reasons given below.



(1) The proton n.m.r. spectrum (Figure 1) has a signal at 8.28 p.p.m. vs. tetramethylsilane in the τ -scale. This must be due to a methyl group attached to an olefinic carbon. The corresponding signal in the 1:1 adduct V from biacetyl and trimethyl phosphite⁶⁻⁸ is at τ 8.25.

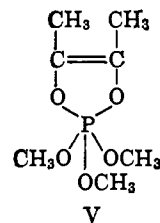


Figure 1 shows that the protons of the methoxyl groups give one doublet. This doublet is due to a coupling between the proton and the phosphorus nuclei. The coupling constant and the position of the doublet at τ 6.58 are very similar to those of the biacetyl adduct⁶ V. The lone benzylic proton gave a doublet at τ 5.96, with $J_{HP} = 24$ c.p.s. The acetyl protons gave a singlet at τ 7.59.

(2) The P^{31} n.m.r. spectrum (Figure 2) corresponds to a phosphorus signal that has been split into two lines by an adjacent proton with a coupling of 24 c.p.s., each one of these two lines being, in turn, split into ten lines by the nine methoxyl protons. Since the latter have a coupling constant of 12 c.p.s., sixteen

(6) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **85**, 3252 (1963).

(7) G. H. Birum and J. L. Dever, Abstracts, Division of Organic Chemistry, 135th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1958, p. 101P.

(8) V. A. Kukhtin and K. M. Kirillova, *J. Gen. Chem. USSR*, **32**, 2755 (1962).

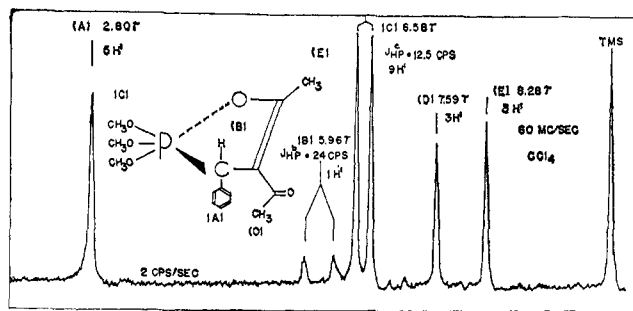


Figure 1.

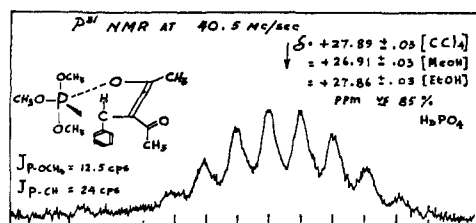


Figure 2.

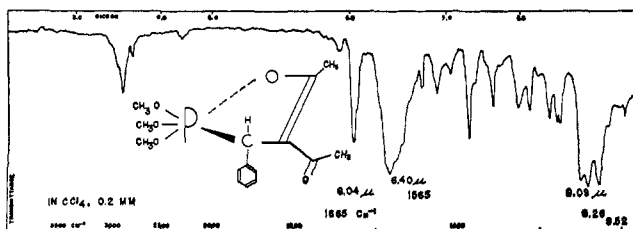


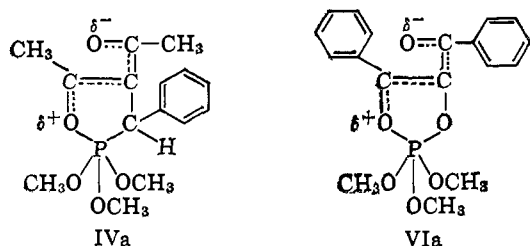
Figure 3.

of the resulting twenty lines will overlap to give eight which added to the remaining four should produce the pattern of twelve lines seen in Figure 2.

The phosphorus in the adduct gave a signal, $\delta_{P11} = +27.9$ p.p.m., at higher magnetic field than 85% H_3PO_4 . Positive chemical shifts are characteristic of pentavalent phosphorus.⁹

Fresh solutions of the adduct IV in alcohols and in carbon tetrachloride gave similar spectra.

(3) The infrared spectrum shown in Figure 3 has the type of $POCH_3$ bands found in other trimethoxyphosphoranes.⁶ These are at 9.09, and 9.26 μ . The band at 6.04 μ is attributed to the olefinic double bond, while the very strong and broad band at 6.40 μ is assigned to the carbonyl group. This band is unusual and should be compared with the band at 6.45 μ found in the 1:1 adduct VIa derived from diphenylpropanetrione and trimethyl phosphite.¹⁰ Structures IVa and VIa,



(9) For documentation see the previous paper.⁶

(10) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Am. Chem. Soc.*, 87 (in press).

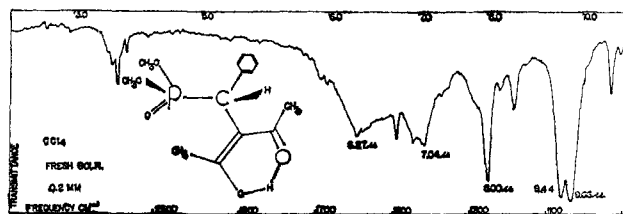


Figure 4.

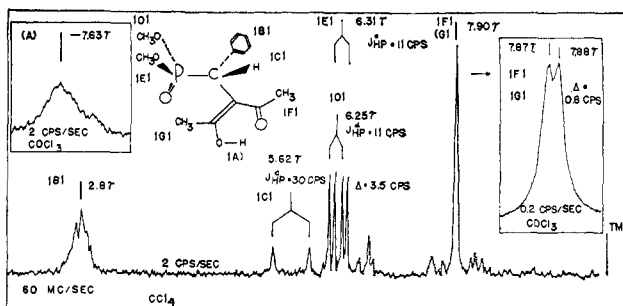
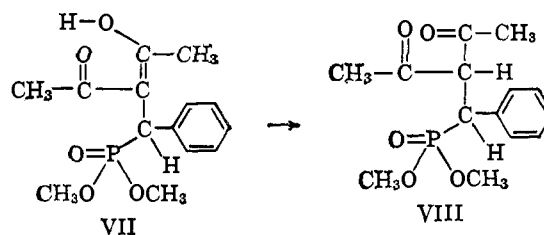


Figure 5.

in which the phosphorus retains its pentavalent character, may contribute to the ground state of the oxyphosphoranes.

The cyclic oxyphosphorane IV does not react with a second molecule of 3-benzylidene-2,4-pentanedione, nor with aliphatic aldehydes. One mole equivalent of water yielded the metastable enol phosphonate VII with the infrared spectrum typical of "conjugate chelation" (Figure 4). The H^1 n.m.r. spectrum (Figure 5)



shows an acidic proton at $\tau -7.63$ and a doublet at 5.62, $J_{HP} = 30$ c.p.s., due to the benzylic proton. Two doublets, τ 6.25 and 6.31, both with $J_{HP} = 11$ c.p.s., result from the two methoxyl groups, which are not magnetically equivalent due to the molecular asymmetry.^{1b} The two methyl groups attached to carbon are magnetically similar (τ 7.90) but not equivalent ($\Delta = 0.8$ c.p.s.).

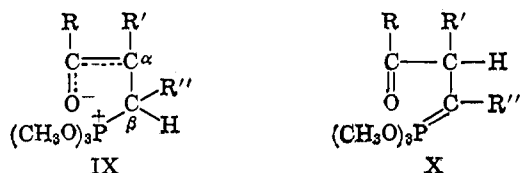
The enol phosphonate VII tautomerized readily to the β -diketone phosphonate VIII which showed the expected infrared spectrum (strong carbonyl at 5.90 μ).

The H^1 n.m.r. spectrum showed the relatively large separation between the two doublets (τ 6.40 and 6.57), $J_{HP} = 11$ c.p.s., due to the two methoxyl groups; and between the two singlets (τ 7.66 and 8.20) due to the two acetyl groups, which result from the molecular asymmetry. The diketone phosphonate VIII had $\delta_{P11} = -27.2$ p.p.m. vs. 85% H_3PO_4 .

Trimethyl phosphite did not react with mesityl oxide, $CH_3 \cdot CO \cdot CH=C(CH_3)_2$, in methylene chloride solution (12 M, 1:1 mole ratio) within 6 days.

Discussion

This and the previous paper^{1b} show that the reaction of triply connected phosphorus compounds with α,β -unsaturated carbonyl compounds may lead to different results depending on the structure of the carbonyl compound. The first step is attack by phosphorus on the β -carbon to give the 1:1 dipolar adduct IX as



shown in the case of *trans*-dibenzoyl ethylene ($R = C_6H_5$, $R' = H$, $R'' = CO \cdot C_6H_5$). Mesityl oxide, with two methyl groups on the β -carbon, failed to react with trimethyl phosphite at 20°.

The dipolar adduct IX may cyclize to a relatively stable oxyphosphorane (IV) or it may undergo a rapid proton transfer to an alkylidenephosphorane (phosphitemethylene, X, $R = C_6H_5$, $R' = H$, $R'' = CO \cdot C_6H_5$). The nature of the substituents, R , R' , and R'' will determine the relative stabilities of the two "anions" IX and X, as well as of the cyclic oxyphosphorane IV. The alkylidenephosphorane X (or the dipolar adduct IX) are capable of reacting with a second molecule of the α,β -unsaturated ketone,^{1b} but it should be noted that the cyclic oxyphosphorane IV failed to react further in this manner.

Evidently, the relative reactivity of IX, X, and IV will be affected also by the nature of the substituents attached to the phosphorus. This point remains for further investigation.

Experimental

The instrumentation employed and the method of calibration of the P^{31} n.m.r. signals have been described.¹¹ Analyses were by Schwarzkopf Micro-analytical Laboratory, Woodside, N. Y. Trimethyl phosphite was dried over sodium and distilled. Methylene chloride was dried over P_2O_5 at 20°, decanted, and distilled.

Reaction of 3-Benzylidene-2,4-pentanedione (III) with Trimethyl Phosphite. Trimethyl phosphite (11.3 g.) was added to a solution of 3-benzylidene-2,4-pentanedione (III, 16.35 g., 1 mole equiv.) in methylene chloride (dry). The solution was kept under nitrogen for 24 hr. at 20°, and for 5 hr. at 40°. The solvent was removed and the residue was dissolved in hexane. (These operations were carried out in the absence of moisture. The oxyphosphorane IV is soluble in hexane while gummy and amorphous; however, upon crystallization, it becomes sparingly soluble in hexane but can be dissolved in benzene.)

The clear hexane solution of the oxyphosphorane was seeded with crystals previously obtained as described below. After 8 hr. at 0°, crystals separated, yielding 25.12 g., m.p. 48–51 in a sealed capillary, 45–48° in an open capillary. The H^1 n.m.r., the P^{31} n.m.r., and the infrared spectra are reproduced in Figures 1, 2, and 3. This material was washed with hexane, dried, and

analyzed as such, although it can be recrystallized further from benzene–hexane.

Anal. Calcd. for $C_{15}H_{21}O_5P$: C, 57.7; H, 6.7; P, 9.9; mol. wt., 312. Found: C, 57.3; H, 6.9; P, 9.8; mol. wt. (isothermal distillation from anhydrous benzene), 314.

Originally, the oxyphosphorane IV was obtained in an amorphous form. The methylene chloride solution was evaporated to dryness (40° at 1 mm.). The residue was dissolved in benzene and again the solvent and any excess of trimethyl phosphite were removed *in vacuo*. The resulting gum was analyzed directly and found to correspond to the oxyphosphorane IV. The infrared, proton, and P^{31} spectra were identical with those of the analytical sample. The gum was allowed to crystallize in hexane solution at 0° for 2 weeks.

Reaction of the 3-Benzylidene-2,4-pentanedione–Trimethyl Phosphite 1:1 Adduct (IV) with Anhydrous Hydrogen Chloride. Formation of Dimethyl (1-Phenyl-2,2-diacetyl)ethylphosphonate (VIII). The 1:1 adduct IV was made from 13.05 g. of the unsaturated ketone III and 8.6 g. of trimethyl phosphite in 50 ml. of dry methylene chloride (16 hr. at 20° under N_2). The solvent was removed at 20° (18 mm.) and the residue was dissolved in dry diethyl ether. The solution was cooled at 0° and treated with hydrogen chloride gas. The crystals that separated (9.17 g.) had m.p. 107–108°. The ether solution was concentrated and allowed to cool to obtain 6.92 g. of more diketo phosphonate VIII of the same melting point; total yield 80%. The analytical sample was obtained from benzene–hexane and melted at 109–110°, $\delta_{P^{31}} = -27.2$ p.p.m. vs. 85% H_3PO_4 . The infrared spectrum (CCl_4) had a strong carbonyl band at 5.92, with a small shoulder at 5.85 μ ; strong PO band at 7.97 μ ; strong double band at 9.43 and 9.71 μ for the $POCH_3$.

Anal. Calcd. for $C_{14}H_{19}O_5P$: C, 56.4; H, 6.4; P, 10.4. Found: C, 56.8; H, 6.6; P, 10.5.

Hydrolysis of the Oxyphosphorane IV with 1 Mole Equiv. of Water. Formation of the Diketo Phosphonate VIII and of Its Enol Tautomer VII. A solution of the oxyphosphorane IV (7.95 g.) in benzene (15 ml.) was treated with 0.45 ml. of water. There was an immediate reaction with elevation of the temperature by 10°. After 15 min. the solution was evaporated to dryness at 45° and 18 mm. The residue was a low-melting solid (7.6 g., m.p. ca. 59–66°) which was immediately stirred with 20 ml. of ether and cooled for 2–3 min. Filtration afforded 4.0 g. of the enol tautomer VII, m.p. 77–81°. This was immediately dissolved in ether and allowed to crystallize at 0°. Immediate filtration gave the analytical sample whose properties were examined within 30 min. The infrared and proton n.m.r. spectra are reproduced in Figures 4 and 5.

Anal. Calcd. for $C_{14}H_{19}O_5P$: C, 56.4; H, 6.4; P, 10.4. Found: C, 56.3; H, 6.6; P, 10.9.

When a solution of the enol VII in ether was treated with dry HCl at 0° for 5 min., complete conversion to the diketo phosphonate VIII was observed, m.p. 103–105°.

The original ether solution from which the 4.01 g. of the enol tautomer VII had been removed was allowed to stand at 0°. The resulting crystals (0.9 g.) were found to contain a mixture of enol and keto tautomers VII and VIII.

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

Methanolysis of the Oxyphosphorane IV. A solution of the oxyphosphorane (6.8 g.) in methanol (15 ml.) was kept at 0°. The infrared spectrum of aliquots of this solution were examined in CCl₄ solution after removal of the methanol. Spectra were taken after 5 min., 90 min. and 6, 25, 31, 97, 121, 147, 173, and 202

hr. The methanolysis at 20° was very slow and after 202 hr. the solvent was removed. The residue was the diketo phosphonate VII, 4.0 g., m.p. 106–108°.

Acknowledgment. We are grateful to Professor P. C. Lauterbur of this department for instruction in P³¹ n.m.r. spectroscopy.

Kinetics and Mechanism of Pertungstic Acid Epoxidations. II. The Methyl-Substituted Allyl Alcohols¹

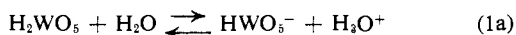
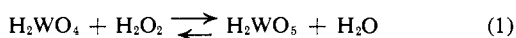
H. C. Stevens and A. J. Kaman

Contribution from the Pittsburgh Plate Glass Company,
Chemical Division, Barberton, Ohio. Received October 7, 1964

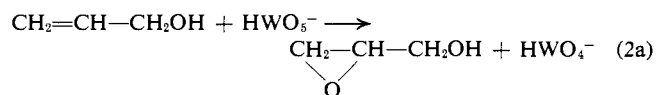
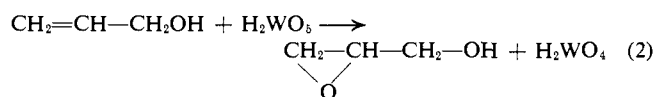
The epoxidation of primary and secondary allylic alcohols by hydrogen peroxide in the presence of tungstic acid appears to involve the formation of a pertungstate ester followed by a rate-determining rearrangement. Based on substituent, solvent, and salt effects, the mechanism of the epoxidation step is believed concerted with considerable polar (electrophilic) character.

Introduction

In a previous paper from this laboratory² we reported on the kinetics of epoxidizing allyl alcohol in buffered aqueous hydrogen peroxide containing tungstic acid as catalyst. The rate was found to be first order in both substrate and catalyst but independent of the hydrogen peroxide concentration. Since tungstic oxide was found to be completely oxidized in the presence of excess hydrogen peroxide, it was surmised that the reacting species was pertungstic acid or a closely related anionic species. Their formation is most simply represented by the following equilibria.



Catalyst regeneration was assumed to be the result of the subsequent epoxidation step



Suggestions concerning mechanisms of oxidations by pertungstate species have been advanced by Mugdan and Young,³ Payne,⁴ Saegebarth,⁵ and Raciszewski.² However, no mechanistic study of the epoxidation

(1) Presented in part at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.

(2) Z. Raciszewski, *J. Am. Chem. Soc.*, **82**, 1267 (1960).

(3) M. Mugdan and D. P. Young, *J. Chem. Soc.*, 2988 (1949).

(4) G. B. Payne, Fifth Petroleum Congress, Section IV, Paper 16, New York, N. Y., 1959.

(5) K. A. Saegebarth, *J. Org. Chem.*, **24**, 1214 (1959).

reaction with a selected group of substrates has been reported.

Two critical approaches were taken in our work to elucidate the mechanism of the epoxidation reaction. First, to assess polar effects in the addition, the substitution of methyl groups onto the three carbon atoms of allyl alcohol was investigated kinetically. Secondly, the importance of the relative proximity of the olefinic and hydroxylic functions upon the reactivity of the substrate was examined with a number of cyclic and acyclic olefin alcohols. This paper pertains to the first of the two objectives.

Experimental

A. Materials. The unsaturated alcohols were commercial samples redistilled before use. Center cuts were collected and assayed by v.p.c. and unsaturation equivalent. The values were recorded in Table I.

Table I

Alcohol	Assay, %		<i>n</i> _D ²⁰
	V.p.c.	Unsatd.	
Allyl	99.6	100.0	1.4150
α-Methallyl	97.2	100.1	1.4147
β-Methallyl	99.9	100.2	1.4267
Crotyl	99.3	...	1.4289
α,α-Dimethallyl	98.1	...	1.4168

B. Kinetic Experiments. In a typical run 0.324 g. (1.3 mmoles) of tungstic acid (Baker analyzed reagent), 23.5 g. (0.339 mole) of 49.01% aqueous hydrogen peroxide (Pittsburgh Plate Glass, Chem. Div.), and 14.9 g. of distilled water were added to a 500-ml., four-necked flask equipped with a Trubone stirrer and immersed in a thermostated water bath controlled at 20 ± 0.1°. The mixture was stirred for 30 min. resulting in a pale blue, turbid solution. Immediately afterwards 0.1–0.2 g. of triethylamine (Eastman Kodak) was introduced to adjust the pH from 2.2 to 4.8–5.0. In the course of 15 sec. 0.300 mole of olefin alcohol freshly dissolved was added in 184.1 g. of distilled water precooled to 20°. This was followed by a 5.0-ml. rinse. A total charge of 249.7 g