

the carbonyl and the donor group. Entropies of activation will also be obtained, and the mechanism of the uncatalyzed reaction will be investigated more fully.

Acknowledgments. The authors are grateful to the Lowell Technological Institute Research Foundation for a grant supporting this work and for assistance in

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A New Approach to the Synthesis of α -Hydroxy- β -diketones and γ -Bromo- α -hydroxy- β -diketones and Their Phosphate Esters

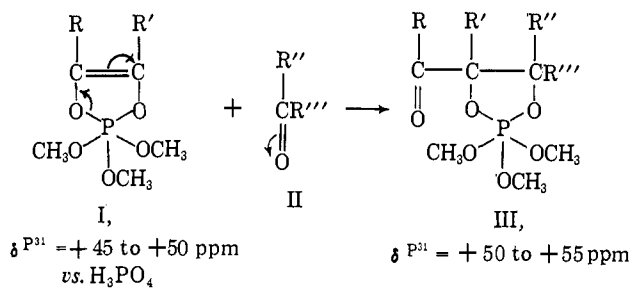
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Received February 10, 1967

Abstract: 2,2,2-Trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene, made from trimethyl phosphite and biacetyl, reacted with ketene, $\text{CH}_2=\text{C}=\text{O}$, and gave 2,2,2-trimethoxy-4-methylene-5-acetyl-5-methyl-1,3,2-dioxaphospholane in over 90% yield. This phospholane was quantitatively converted by hydrogen chloride into the dimethyl phosphate ester of 3-methylpentan-3-ol-2,4-dione (diacetylmethylcarbinol). The phosphorus-free hydroxydiketone was made from the phospholane or the phosphate in boiling aqueous benzene. Bromination of the phospholane gave the dimethyl phosphate ester of 1-bromo-3-methylpentan-3-ol-2,4-dione.

The formation of a carbon-carbon single bond by the nucleophilic addition of a 2,2,2-trialkoxy-1,3,2-dioxaphospholene² (I) to a carbonyl function II was first reported in 1961.³ This condensation reaction made available the new 2,2,2-trialkoxy-1,3,2-dioxaphospholanes⁴ (III).



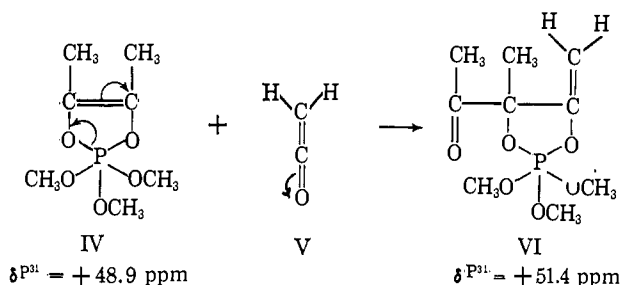
The phospholanes III could be transformed into cyclic and open-chain phosphate esters, and into phosphorus-free polyoxygenated functions.⁵ Some of the phospholanes were also capable of undergoing molecular rearrangements when heated in methanol solution.^{4,6}

This paper describes the condensation of a phospholene I with ketene,⁷ and discloses a new approach to the

synthesis of α -hydroxy- β -diketones and γ -bromo- α -hydroxy- β -diketones and their phosphate esters.

Results

Reaction of Ketene with the Trimethyl Biacetylphosphite 1:1 Adduct IV. The reaction of ketene V with 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (IV) took place at 0° in methylene chloride solution. The product was 2,2,2-trimethoxy-4-methylene-5-acetyl-5-methyl-1,3,2-dioxaphospholane (VI) isolated in 90% yield.



The phospholane VI probably arose in a concerted nucleophilic addition of the phospholene IV to the ketene V without the formation of an intermediate dipolar ion like VII.⁸ However, the transient formation of undetectably small amounts of VII cannot be excluded.

The pentaoxyphosphorane VI was distinguished from the isomeric tetraoxyalkylphosphorane VIII on the basis of the following spectral data.

(7) While this work was in progress, A. J. Kirby [*Tetrahedron*, **22**, 3001 (1966)] published experiments involving the phospholene IV and carbon disulfide. Our studies of the reactions of IV, and of related phospholenes, with a number of systems having cumulated double bonds will be published in a separate communication.

(8) (a) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **30**, 2575 (1965); (b) *ibid.*, **31**, 474 (1966).

(1) 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-6690-Y.

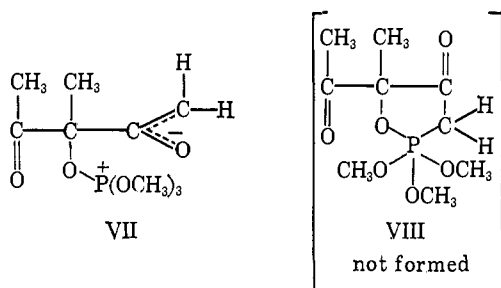
(2) For a review, see F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).

(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); (c) F. Ramirez, N. B. Desai, and N. Ramanathan, *Tetrahedron Letters*, 323 (1963).

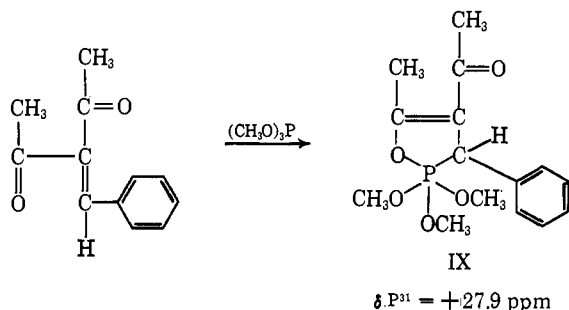
(4) For a review, see F. Ramirez, *Bull. Soc. Chim. France*, 2443 (1966).

(5) (a) F. Ramirez, A. V. Patwardhan, N. B. Desai, and S. R. Heller, *J. Am. Chem. Soc.*, **87**, 549 (1965); (b) F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963); (c) F. Ramirez, S. B. Bhatia, and C. P. Smith, *Tetrahedron*, in press.

(6) F. Ramirez, H. J. Kugler, and C. P. Smith, *Tetrahedron Letters*, 261 (1965).



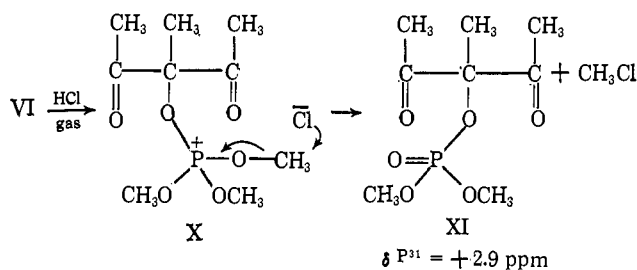
(1) The P^{31} nmr shift, δP^{31} , of VI was very close to that found for other related pentaoxyphosphoranes^{4,9} of type III. On the other hand, the tetraalkoxyphosphorane IX gave a signal at a much lower magnetic field.¹⁰



(2) The H^1 nmr spectrum of VI, examined at 60 and 100 Mc/sec, had one-proton signals at τ 5.80 and 6.21. Both signals consisted of doublets of doublets. The coupling between the two vinyl protons was $J_{HH} = 1.9$ cps. One of the hydrogen-phosphorus couplings was $J_{HP} \sim 1.9$ cps and, therefore, the signal looked like a distorted triplet. The other J_{HP} value was approximately 1.4 cps. These values were in agreement with structure VI but not VIII. The three indistinguishable methoxy groups gave one doublet at τ 6.40, $J_{HP} = 13$ cps. The acetyl and the methyl protons were at τ 7.82 and 8.50, respectively.

(3) The infrared spectrum of VI had the expected bands at 5.80 and 6.00 μ due to the acetyl and the enol phosphorane, respectively.¹¹

Reaction of the Phospholane VI with Hydrogen Chloride. This reaction afforded the dimethyl phosphate ester of 3-methylpentan-3-ol-2,4-dione (XI) in quantitative yield. Probably, a tetraalkoxyphosphonium chloride X was an intermediate.



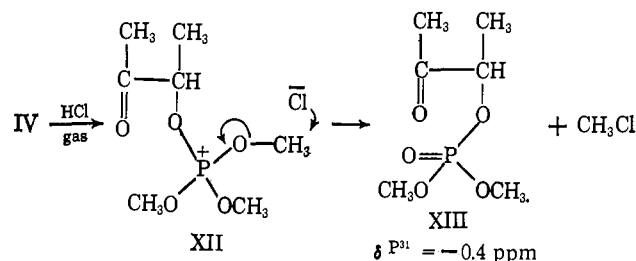
The reaction can be considered as an alkylation of hydrogen chloride by the unsaturated phospholane

(9) For open-chain pentaoxyphosphoranes, see D. B. Denney and S. T. D. Gough, *J. Am. Chem. Soc.*, **87**, 138 (1965), and references therein.

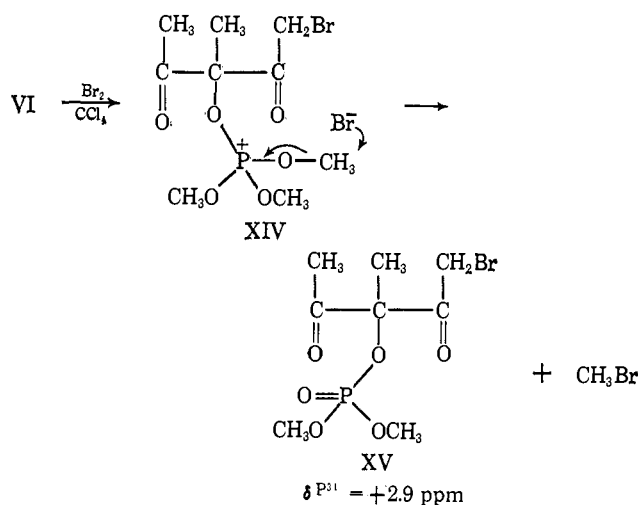
(10) F. Ramirez, O. P. Madan, and S. R. Heller, *ibid.*, **87**, 731 (1965).

(11) The spectrum of VI had a strong band at 12.0 μ , which could be due to the hydrogen out-of-plane deformations of the vinyl group; see L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 51.

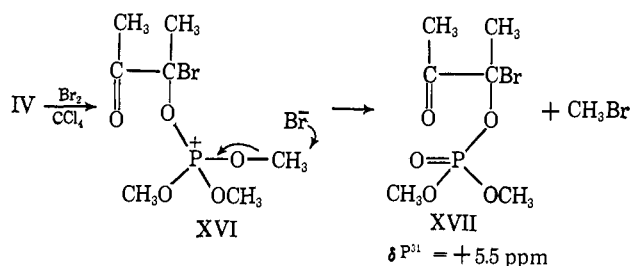
VI. A similar alkylation by the phospholene IV was previously reported¹² and is shown in formulas XII \rightarrow XIII.



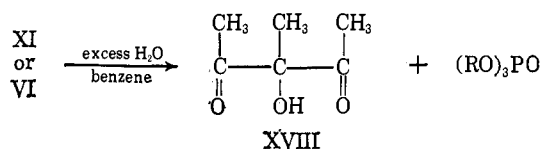
Reaction of the Phospholane VI with Bromine. This reaction was carried out in CCl_4 solution at 0° and gave α -bromo- α -hydroxy- β -diketone XV in quantitative yield.



A possible mechanism is shown in formula XIV. It should be noted that the bromination of the phospholene IV gave α -bromo- α -ketol phosphate¹² XVII, probably by a similar path.



Hydrolysis of the α -Hydroxy- β -diketone Phosphotriester XI. The phosphotriester XI was converted into 3-methylpentan-3-ol-2,4-dione or diacetylmethylcarbinol^{13,14} (XVIII) by aqueous benzene at 80°.

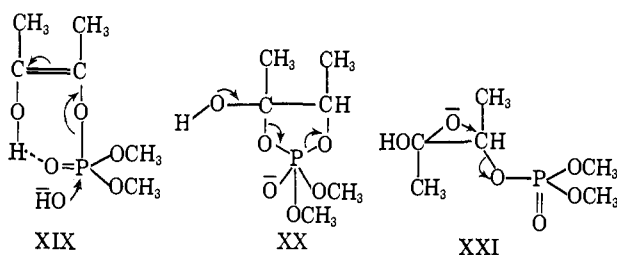


(12) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **82**, 2652 (1960).

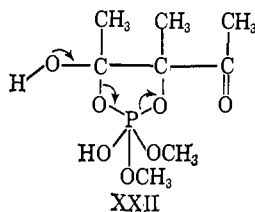
(13) "Water solutions" of diacetylmethylcarbinol have been described (*cf.* ref 14). The pure alcohol was not isolated, and, consequently, analytical data were not provided. The bis(2,4-dinitrophenylhydrazine) was said to melt at 234–238°. The water solutions of the alcohol were made by acid hydrolysis of its acetate, which was prepared from α -methyl- α -acetylacetone and lead tetraacetate.

(14) (a) E. Juni and G. Heym, *Arch. Biochem. Biophys.*, **67**, 410 (1957); (b) E. Juni and G. Heym, *J. Biol. Chem.*, **218**, 365 (1956).

This is a remarkably facile hydrolysis; trimethyl phosphate, or even dimethylphosphoacetoin (XIII), was not affected by water in boiling benzene, under comparable conditions. We have shown¹⁵ that the second-order rate constant for the *hydroxide ion catalyzed* conversion of dimethylphosphoacetoin (XIII) into acetoin and dimethyl hydrogen phosphate was $k_2 = 360 \text{ l. mole}^{-1} \text{ sec}^{-1}$, at 25°, in water at pH 7.7–8.3. This was at least 2×10^6 times faster than the corresponding value for trimethyl phosphate. Two possible explanations were proposed for this rate difference. (1) The acceleration could be due to the unsaturated nature of the leaving group and to hydrogen-bonding assistance (formula XIX). (2) The effect might result from carbonyl participation and oxyphosphorane formation during the hydrolysis (formula XX). Subsequently, a third explanation involving a hydroxyepoxide intermediate was proposed¹⁶ (formula XXI).



Rate data for the hydroxide ion catalyzed hydrolysis of the hydroxydiketone phosphate XI are not available yet. However, it seems at least possible, that the extraordinarily rapid hydrolysis in aqueous benzene might involve the oxyphosphorane intermediate XXII.



Hydrolysis of the Phospholane VI. The phospholane VI was readily converted into diacetylmethylcarbinol (XVIII) by an excess of water in benzene solution at 80°.

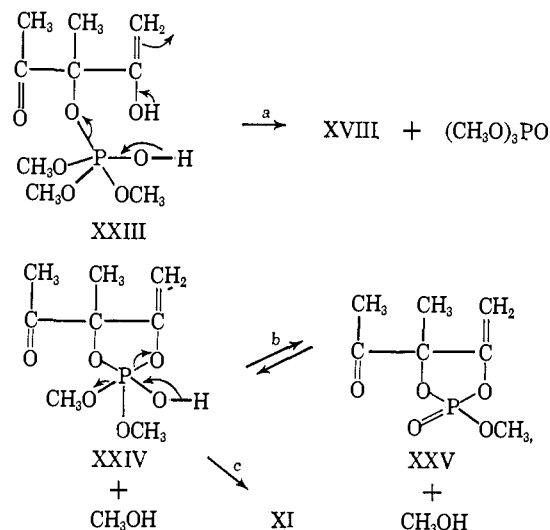
When 1 molar equiv of water, or of D₂O, was added to a solution of the phospholane VI in benzene, or in deuteriochloroform, four substances were produced almost instantaneously at 20°, or even at 0°. These were trimethyl phosphate, the hydroxydiketone XVIII, the dimethyl phosphate ester XI derived from this alcohol, and methanol. There was no evidence for the formation of the cyclic phosphotriester XXV. These conclusions were reached by an examination of the P³¹ and the H¹ nmr data of the solutions at various times. These results are explained in terms of the intermediates XXIII and XXIV.

Support for the formation of intermediates like XXIII and XXIV has been adduced previously.^{17–19}

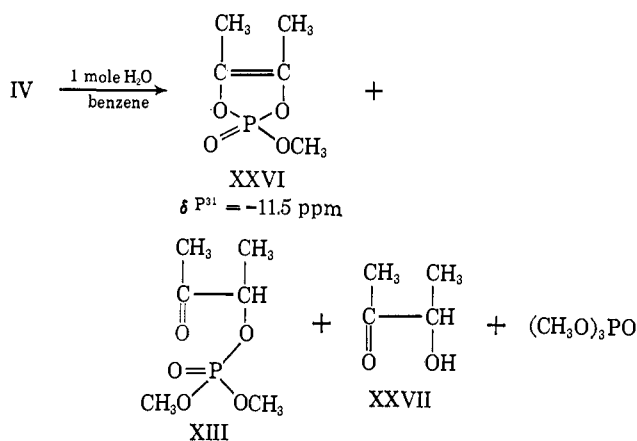
(15) F. Ramirez, B. Hansen, and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 4588 (1962).

(16) (a) H. Witzel, A. Botta, and K. Dimroth, *Ber.*, **98**, 1465 (1965); (b) T. C. Bruice and S. J. Benkovic, "Biorganic Mechanisms," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, p 104, have recently discussed this problem.

(17) F. Ramirez, O. P. Madan, and C. P. Smith, *J. Am. Chem. Soc.*, **87**, 670 (1965).



In particular, it should be noted that the hydrolysis of the phospholane IV gave trimethyl phosphate, acetoin, dimethylphosphoacetoin (XIII), *acetoinediol cyclophosphate* (XXVI), and methanol. The relative proportion of these products could be greatly altered by changes in temperature and other experimental conditions.¹⁷



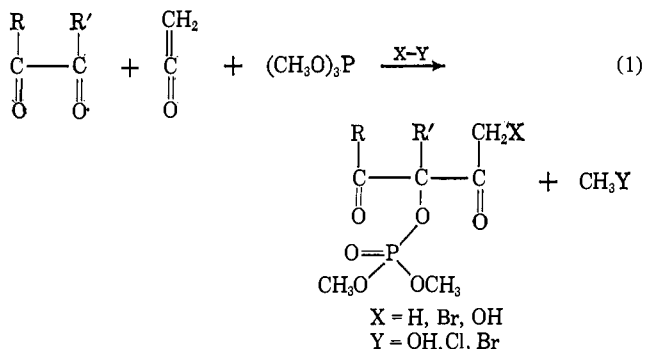
Discussion

The condensation of α -dicarbonyl compounds with ketenes by means of trialkyl phosphites opens a new route to a variety of polyoxygenated functions related to the carbohydrates. The phosphate esters of these sugar-like materials can also be obtained in this manner (eq 1).

The various steps in these transformations can be carried out rapidly and under exceptionally mild conditions. The final products can be isolated easily and in high yields. Experiments are now under way to delimit the scope of these reactions in terms of (1) variations in the structure of the carbonyl compounds and the ketenes; (2) further transformations of the

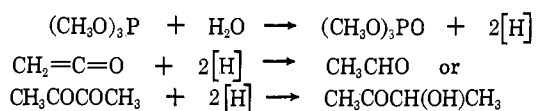
(18) (a) F. Ramirez, N. B. Desai, and N. Ramanathan, *ibid.*, **85**, 1874 (1963); (b) F. Ramirez, O. P. Madan, N. B. Desai, S. Meyerson, and E. M. Banas, *ibid.*, **85**, 2681 (1963).

(19) The formation of an *intermediate* (rather than a transition state) with quintuply connected phosphorus, which we have advocated to explain our observations on the hydrolysis of pentaoxyphosphoranes and of five-membered cyclic phosphotriesters (see ref 17 and 18), has been recently proposed also by Westheimer and co-workers to account for their observations during a comprehensive study of the hydrolysis of cyclic phosphates, phosphonates, and phosphinates; see E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3431, 3432 (1966), and previous references given there.

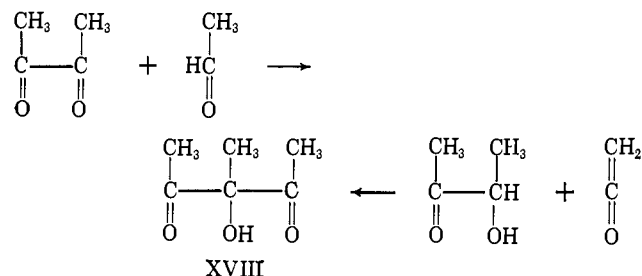


carbonylketene phosphite adducts to polyfunctional phosphorus-free materials; (3) synthesis of new types of polyfunctional phosphate esters and further transformations of them.

It should be noted that the combination of the oxyphosphorane condensation with a hydrolytic step accomplishes the following objective²⁰



Formally, the reductive phosphorylation of the α -dicarbonyl compound by a phosphite ester in the presence of ketene amounts to a condensation between biacetyl and acetaldehyde, or its equivalent, acetoin and ketene.



Diacetylmethylcarbinol (XVIII) and acetoin were reported to be formed simultaneously when biacetyl was used as the substrate for the enzyme pyruvic oxidase.^{14,21}

Experimental Section

The analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The instrumentation was described previously.⁴ All P^{31} nmr shifts are given in parts per million from 85% H_3PO_4 as zero; they were determined at 40.5 Mc/sec. All H^1 nmr shifts are given in parts per million from TMS as 10 (τ values); they were determined at 60 or at 100 Mc/sec, as indicated.

Reaction of Ketene with 2,2,2-Trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (IV). Ketene was bubbled through a stirred solution of the phospholene IV (95 g) in methylene chloride (75 ml) kept in an ice bath. H^1 nmr analysis showed the complete disappearance of IV within 1.5 hr. The solvent and some of the acetone introduced with the ketene were removed at 20°, first at 20 mm, then at 1 mm. The residue was distilled through a 6-in. Vigreux column. Fraction 1 (19 g) was collected below 55° (0.3 mm) and consisted of the adduct VI contaminated with some trimethyl phosphite. Fraction 2 (85 g) was 2,2,2-trimethoxy-4-methylene-5-acetyl-5-methyl-1,3,2-dioxaphospholane (VI), bp 56–57° (0.1 mm). The spectral characteristics of this material did not change after redistillation. A sample fractionated through a 24-in. spinning-

band column had bp 62° (0.2 mm); prolonged heating may lead to partial decomposition.

Anal. Calcd for $\text{C}_9\text{H}_{17}\text{O}_6\text{P}$: C, 42.9; H, 6.7; P, 12.3; mol wt, 252. Found: C, 42.5; H, 6.8; P, 12.1; mol wt, 247.

The P^{31} nmr spectrum (neat liquid) had a multiplet at +51.4 ppm vs. H_3PO_4 . The H^1 nmr spectrum in CDCl_3 had a 1 H^1 doublet of doublets at τ 5.80, $J_{\text{HH}} = 1.9$ cps, $J_{\text{HP}} = 1.9$ cps, and a second 1 H^1 doublet of doublets at τ 6.21, $J_{\text{HH}} = 1.9$ cps, $J_{\text{HP}} = 1.4$ cps; the separation between the centers of these two multiplets was 23 cps at 60 Mc/sec and 39 cps at 100 Mc/sec. The spectrum had also a 9 H^1 doublet at τ 6.40, $J_{\text{HP}} = 13$ cps, and 3 H^1 singlets at τ 7.82 and 8.50, respectively. Better resolution was achieved in benzene, where the signals were at τ 5.80, 6.20, 6.45, 7.88, and 8.52, respectively. The low-field vinyl phosphorane protons had the appearance of a distorted triplet in all solvents.

The infrared spectrum (CH_2Cl_2) had bands (μ) at 3.43 (w), 3.55 (w), 5.80 (s) ($\text{C}=\text{O}$), 6.00 (m) ($\text{C}=\text{CO}$), 6.90 (w), 7.30 (w), 7.40 (w), 7.75 (m), 8.50 (m), 8.60 (m), 9.20 (vs) (POCH_3), 10.00 (vs), 10.45 (w), 11.42 (m), 12.00 (s) (probably H out-of-plane deformation of $\text{OC}=\text{CH}_2$, with shoulder at 11.85), and 12.90 (ms).

Redistillation of fraction 1 using a 12-in. spinning-band column gave an additional amount of adduct VI, which was formed in about 90% yield. The H^1 nmr of the original distillation residue showed the presence in it of more adduct VI.

Reaction of the Phospholane VI with Hydrogen Chloride. Anhydrous hydrogen chloride was passed through a solution of the dioxaphospholane VI (19 g) in methylene chloride (50 ml) at 0° until saturation was achieved. The solvent was removed at 20° (20 mm); the H^1 nmr spectrum of the crude residue showed the presence of nearly pure diketo phosphate XI. Short-path distillation gave pure 3-methylpentan-3-ol-2,4-dione dimethyl phosphate (XI), bp 87° (0.1 mm), yield 17 g (90%), n_D^{25} 1.4358; δP^{31} (in CDCl_3) = +2.9 ppm, a septet.

Anal. Calcd for $\text{C}_8\text{H}_{15}\text{O}_6\text{P}$: C, 40.3; H, 6.30; P, 13.0. Found: C, 40.8; H, 6.5; P, 12.6.

The H^1 nmr spectrum in CDCl_3 had a 6 H^1 doublet at τ 6.18, $J_{\text{HP}} = 11$ cps (CH_3O), a 6 H^1 singlet at τ 7.75 (acetyl), and a 3 H^1 singlet at τ 8.25 (methyl). No major differences were observed in benzene solution. The infrared spectrum (CH_2Cl_2) had bands at 3.45 (w), 5.80 (s), 5.85 (s) ($2\text{C}=\text{O}$), 6.95 (w), 7.42 (m), 7.85 (s), (PO), 8.45 (w), 9.58 (vs) (POCH_3), 9.85 (s), 11.70 (s) μ .

Reaction of the Phospholane VI with Bromine. A solution of bromine (11.4 g, 71 mmoles) in CCl_4 (25 ml) was added over a period of 1 hr to a stirred solution of the phospholane VI (18 g, 71 mmoles) in CCl_4 (50 ml) at 0°. The colorless solution was evaporated at 20° (20 mm). The residue gave only one P^{31} nmr signal at ± 2.6 ppm (in CH_2Cl_2); the H^1 nmr spectrum was very similar to that of the distilled bromoketo phosphate XV. The analytical sample of 1-bromo-3-methylpentan-3-ol-2,4-dione dimethyl phosphate (XV) was obtained as a pale yellow oil, n_D^{25} 1.4697, after short-path distillation; the approximate boiling point was 106–108°. XV was obtained in nearly quantitative yield. The material slowly turns pink and then reddish brown on prolonged standing at 20°, δP^{31} (CDCl_3) = +2.9 ppm, septet.

Anal. Calcd for $\text{C}_8\text{H}_{14}\text{O}_6\text{BrP}$: C, 30.3; H, 4.4; Br, 25.3; P, 9.7. Found: C, 29.9; H, 4.5; Br, 24.6; P, 9.3.

The H^1 nmr spectrum in CDCl_3 had a 2 H^1 singlet at τ 5.58 (CH_2Br); a 3 H^1 doublet at τ 6.16, $J_{\text{HP}} = 11.5$ cps (CH_3OP), and a second 3 H^1 doublet with about the same coupling constant displaced 0.6 cps to higher field (CH_3OP); a 3 H^1 singlet at τ 7.67 (acetyl); and a 3 H^1 singlet at τ 8.15 (methyl). The infrared spectrum (CH_2Cl_2) had bands at 5.70 (s), 5.80 (s) ($2\text{C}=\text{O}$), 6.90 (m), 7.30 (m), 7.40 (m), 7.80 (s) (PO), 8.40 (m), 8.80 (m), 9.4–9.6 (vs) (POCH_3), and 11.65 (s).

Hydrolysis of 3-Methylpentan-3-ol-2,4-dione Dimethyl Phosphate (XI). Water (20 ml, 15 molar equiv) was added to a solution of the phosphate ester XI (19 g) in benzene (70 ml). The mixture was kept 6 hr at reflux. The water layer was separated and extracted with two 40-ml portions of benzene. The benzene extracts and the original benzene layer were combined, dried over MgSO_4 , and distilled through a 6-in. Vigreux column to remove benzene (care should be exercised to avoid loss of product XVIII). The spectral analysis of the crude oil showed only one component, the hydroxydiketone XVIII. The analytical sample of 3-methylpentan-3-ol-2,4-dione or diacetylmethylcarbinol¹³ (XVIII) had bp 43° (4.5 mm), n_D^{25} 1.4272. XVIII was obtained in 67% yield.

Anal. Calcd for $\text{C}_8\text{H}_{16}\text{O}_3$: C, 55.3; H, 7.8. Found: C, 55.7; H, 7.9.

The H^1 nmr spectrum in CDCl_3 had a 1 H^1 singlet at τ 5.14 (OH), a 6 H^1 singlet at τ 7.76 (acetyl), and a 3 H^1 singlet at τ 8.48 (methyl).

(20) (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **23**, 778 (1958);
 (b) F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **81**, 587 (1959);
 (c) F. Ramirez, E. H. Chen, and S. Dershowitz, *ibid.*, **81**, 4338 (1959).
 (21) R. P. Hullin and H. Hassall, *Biochem. J.*, **83**, 298 (1962).

The infrared spectrum in CH_2Cl_2 had bands at (μ) 2.92 (OH), 5.85 (CO), 7.40, 8.35, and 8.70.

Reaction of the Phospholane VI with an Excess of Water. Water (8 ml, 462 mmoles) was added to a solution of the phospholane VI (15 g, 58 mmoles) in benzene (50 ml). The mixture was kept 4 hr at reflux. The water layer was extracted with benzene. The combined benzene extracts and original solution were fractionated as before. Diacetylmethylcarbinol (XVIII) was isolated in 75% yield.

Reaction of the Phospholane VI with 1 Molar Equiv of Water.
a. In CDCl_3 Solution. Water (1 molar equiv) was added to a solution of the phospholane VI in CDCl_3 at 20° . After the vigorous exothermic reaction had subsided, the solution was analyzed by P^{31} nmr spectrometry at 40.5 Mc/sec. Only the signals due to trimethyl

phosphate and to diacetylmethylcarbinol dimethyl phosphate (XI) were observed. The experiment was repeated using D_2O and a 6 *M* solution of the phospholane VI in CDCl_3 ; the H^1 nmr after 5 min had the signals due to trimethyl phosphate, the deuteriodiacetylmethylcarbinol (XVIII), the open phosphotriester XI, and deuteriomethanol.

b. In Benzene Solutions. Water (1 molar equiv) was added to a 2 *M* solution of phospholane VI in benzene at 0° . The solvent was removed after *ca.* 1 min at 0° (3 min). The residue was dissolved in CDCl_3 . The P^{31} and H^1 nmr spectra showed the signals of the species mentioned above plus those of some unreacted phospholane VI. There was no evidence for the formation of the cyclic phosphate ester XXV.

A New Synthesis of 5-Acylhydantoins, Precursors of β -Keto- α -amino Acids

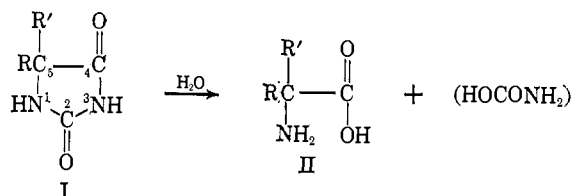
Fausto Ramirez,¹ S. B. Bhatia, and C. P. Smith

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Received February 21, 1967

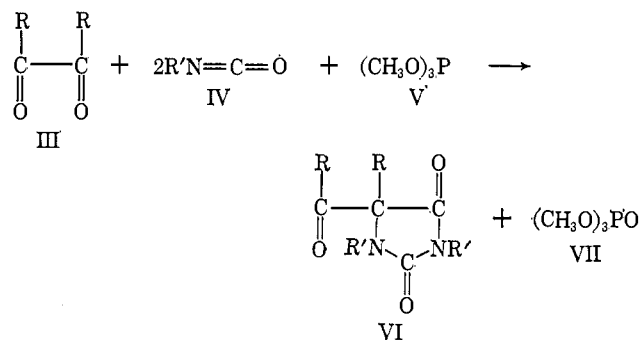
Abstract: A new reaction leading to 5-acylhydantoins, the precursors of β -keto- α -amino acids, is described. In this reaction, a trialkyl phosphite induces the condensation of one molecule of an α -diketone with two molecules of an aryl isocyanate with formation of the 5-acylhydantoin and a trialkyl phosphate. Three steps are involved, and the intermediates can, but need not, be isolated. The intermediates are organic compounds with pentacovalent phosphorus as shown by P^{31} nmr spectroscopy.

The hydantoins I are one of the classical synthetic precursors of the α -amino acids² II.



This type of heterocycle is associated with powerful anticonvulsant action; for example, 5,5-diphenylhydantoin (Dilantin) is widely used in the control of epilepsy.² Consequently, many alkyl- and arylhydantoins have been prepared.² On the other hand, the 5-acylhydantoins, which are the precursors of β -keto- α -amino acids, have not received much attention.^{2c} Modifications of the carbonyl function of the 5-acetylhydantoins prior to hydrolysis would make available a variety of β -substituted α -amino acids.

This paper describes a new approach to 5-acylhydantoins VI based on the condensation of an α -dicarbonyl compound III with an isocyanate³ IV under the influence of a trialkyl phosphite^{4,5} V.



Results

The 2,2,2-trialkoxy-1,3,2-dioxaphospholene⁶ (VIII), prepared from biacetyl and trimethyl phosphite, reacted with phenyl isocyanate (IX) at 30° . The course of the reaction was followed by means of infrared and H^1 and P^{31} nmr spectroscopy. Two distinct steps were observed. The first step was the nucleophilic addition of a carbon atom of the phospholene VIII to the carbonyl carbon of the isocyanate. The product was 2,2,2-trimethoxy-4-phenylimino-5-acetyl-5-methyl-1,3,2-dioxaphospholane (X).

Open-Chain Organic Nitrogen Compounds," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 6.

(4) The deoxygenation of alkyl isocyanates by trialkyl phosphites at elevated temperatures (180 – 190°) has been reported: *cf.* T. Mukaiyama, H. Nambu, and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962).

(5) The formation of certain 2-iminoxazolidines and 2-imidazolidones from the reaction of aryl isocyanates with ethyl bis(β -aminoethyl)-phosphite has been described: *cf.* O. Mitsunobo, T. Ohashi, and T. Mukaiyama, *Bull. Chem. Soc. Japan*, **39**, 708 (1966).

(6) The literature has been reviewed by F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).

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