

(58 mg), and after recrystallization from ethanol amounted to 24.8 mg of compound 19: mp 158–159°; $[\alpha]_D^{20}$ 108.5° (*c* 1.0, CH₃OH). This material was identical in all respects with earlier preparations from mesylate 12 and brosylate 13.

Registry No.—5, 22932-29-2; 6, 22932-30-5; 8, 22932-31-6; 9, 22932-32-7; 10, 22932-33-8; 11, 22932-34-9; 12, 10503-85-2; 13, 10503-86-3; 14, 10515-99-8;

15, 22932-38-3; 16, 15814-59-2; 19, 10503-88-5; 21, 10503-87-4.

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The Photochemical Reactions of α -Ketophosphonates¹

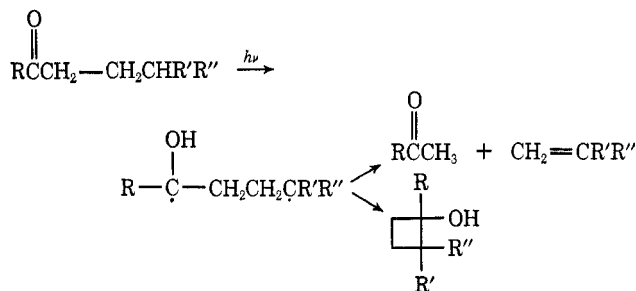
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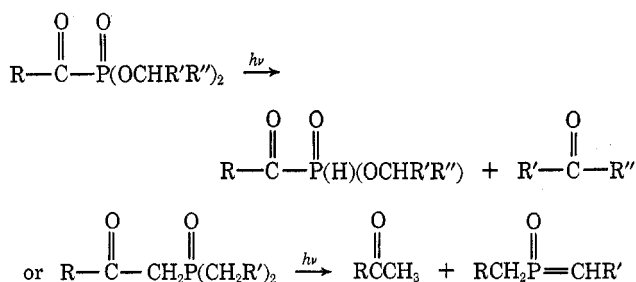
Received July 17, 1969

Irradiation of dialkyl α -ketophosphonates possessing tertiary γ -hydrogens (1c–1e) in benzene affords novel rearrangement products, *i.e.*, half-esters of β -ketophosphonates (2c–2e, 75–91%), together with the products derived from type I cleavage, *i.e.*, dialkyl phenylphosphonates (3c–3e, 2.5–4.0%). However, the similar photolysis of esters possessing primary or secondary γ hydrogens (1a–1b) gives much lower yields of rearrangement products (2a–2b, 0–21.5%) and moderately higher yields of dialkyl phenylphosphonates (3a–3b, 24.6–6.3%). Photoelimination and/or cyclization products are not detected. This reaction is discussed in terms of geometrical and stereoelectronic requirements for intramolecular hydrogen abstraction and type II elimination, a plausible mechanism being postulated.

The carbonyl group plays an important role as a chromophore in organic photochemical reactions. In the condensed phase the major pathway for carbonyl compounds possessing γ hydrogens is photoelimination (type II) to form olefins and smaller carbonyl compounds. This is accompanied by cyclization to form cyclobutanols.²



As an extension of the studies on photochemical reactions of organophosphorus compounds,³ this photoelimination was applied⁴ to ketophosphorus compounds with γ hydrogens, but no reaction such as



(1) Contribution No. 141.

(2) Two comprehensive reviews: (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, pp 377–427; (b) N. C. Yang, "Reactivity of the Photoexcited Organic Molecule," Interscience Publishers, Inc., New York, N. Y., 1967, pp 146–163.

(3) H. Tomioka, Y. Izawa, and Y. Ogata, *Tetrahedron*, **24**, 5739 (1968); **25**, 1501 (1969).

(4) The photoreactions of ketones with γ hydrogens containing a heteroatom such as oxygen⁵ or sulfur⁶ have been reported.

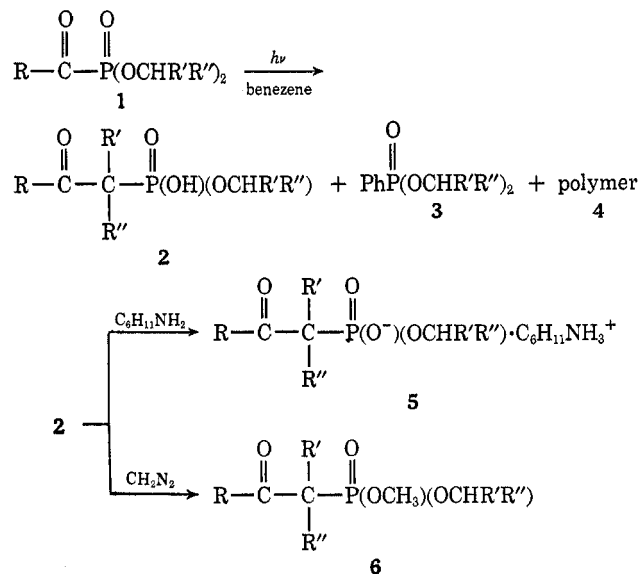
(5) (a) P. Yates and A. G. Szabo, *Tetrahedron Lett.*, 485 (1965); (b) N. J. Turro and F. D. Lewis, *ibid.*, 5845 (1968).

(6) (a) R. B. LaCount and C. E. Griffin, *ibid.*, 1549 (1965); (b) C. L. McIntosh and P. de Mayo, *ibid.*, 37 (1967).

occurred. Instead, anomalous and interesting behavior was observed, which included a novel rearrangement instead of elimination. The present paper outlines this reaction and examines this behavior in terms of factors influencing internal hydrogen abstraction and photoelimination.

Results and Discussion

Irradiation of diisopropyl acetylphosphonate (1c, R = R' = R'' = CH₃) in benzene with ultraviolet light from an unfiltered high-pressure Hg lamp in a quartz or Pyrex tube afforded viscous liquid with rapid consumption of the starting material. (For numbering of compounds, see Table II.) The infrared spectrum of the oil thus obtained showed the strong and broad band of P–OH. The addition of cyclohexylamine to the oil gave a solid (5c), which was identified as an isomer of 1c by elemental analysis and titration. Chromatographic separation of the products after treatment with diazomethane gave two oily substances, which were shown to be 6c (methyl ester of 2c) and 3c on



the basis of nmr and ir spectral data, and an uncharacterized viscous material which appeared to be a polymer (4). The structure of **6c** ($R = R' = R'' = CH_3$) was most strongly supported by comparing the acetyl and isopropyl methyl hydrogen resonance in the nmr spectra of **1c** and **6c** (Figure 1). The acetyl proton of **6c** at τ 6.67 was in marked contrast to that of **1c**, whose signals were split by the ^{31}P nucleus,⁷ indicating rearrangement of acetyl group from the α to the β position of the phosphoryl group, where no such coupling between ^{31}P and the proton is operative. The isopropyl methyl proton of **1c** at τ 8.63 (d) changed into two doublets at τ 8.63 and 8.65 with different coupling constants ($J = 18.0$ and 6.0 cps, respectively) in **6c**, suggesting the insertion of one of isopropyl groups into the C-P bond.

Similar products were obtained in the photolysis of other acylphosphonates, the yield of **2** decreasing in the order of isopropyl, ethyl, and methyl present as the ester group (see Table I).

TABLE I
PHOTOREACTIONS OF ACYLPHOSPHONATES

No.	Compd			Irradn time, hr	% yield ^a		
	R	R'	R''		2	3	4 ^b
1a ^c	CH ₃	H	H	20	0	24.6	67.6
1b	CH ₃	CH ₃	H	4	12.4 (21.5)	6.3	72.8
1c	CH ₃	CH ₃	CH ₃	4	83.5 (90.8)	2.5	5.3
1c ^d	CH ₃	CH ₃	CH ₃	4	(31.2)		
1c ^e	CH ₃	CH ₃	CH ₃	4	(15.3)		
1c ^f	CH ₃	CH ₃	CH ₃	5	(86.3)		
1d	CH ₃	CH ₃	CH ₂ CH ₃	4	72.6 (87.5)	4.0	11.3
1e	Ph	CH ₃	CH ₃	4	75		

^a Yields in parentheses were determined by alkalimetric titration. Other indicated yields are for isolated products. ^b Weight per cent. ^c PhCOCH₃ was detected. ^d In isopropyl alcohol. ^e In air-saturated benzene. ^f In a Pyrex tube.

Neither carbonyl compounds derived from type II elimination nor other low boiling products were detected even in the irradiation at 80° , where the carbon analog, benzoylformate, undergoes efficient elimination.⁸ Cyclization products were also not detected, although α -dicarbonyl compounds such as 5,6-decanedione give exclusively 2-hydroxycyclobutanones.⁹ Neither type II elimination nor cyclization was observed in the photolysis of the other ketophosphorus compounds such as carbethoxyphosphonates (**1g-1h**), α -ketophosphinate (**1i**), β -ketophosphinate (**1j**), and α -ketophosphine oxide (**1k**), where products with a P-OH bond, whose detailed structure has not yet been elucidated, were also formed. Furthermore, products derived from cleavage at the bond β to the carbonyl were not detected in the irradiation of β -ketophosphinate (**1j**), although this photolytic cleavage is predominant in the photolysis of β -keto sulfones.⁶

The decline in rate of the formation of **2** in irradiation in air-saturated benzene suggested that the reactive state is a triplet. In addition, reaction in a Pyrex tube ($>300 m\mu$) gave the same products as reaction in a quartz tube, implying that the primary process is

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(8) E. S. Huyser and D. C. Neckers, *J. Org. Chem.*, **29**, 276 (1964).

(9) W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Lett.*, 609 (1962); W. H. Urry and D. J. Trecker, *J. Amer. Chem. Soc.*, **84**, 118 (1962).

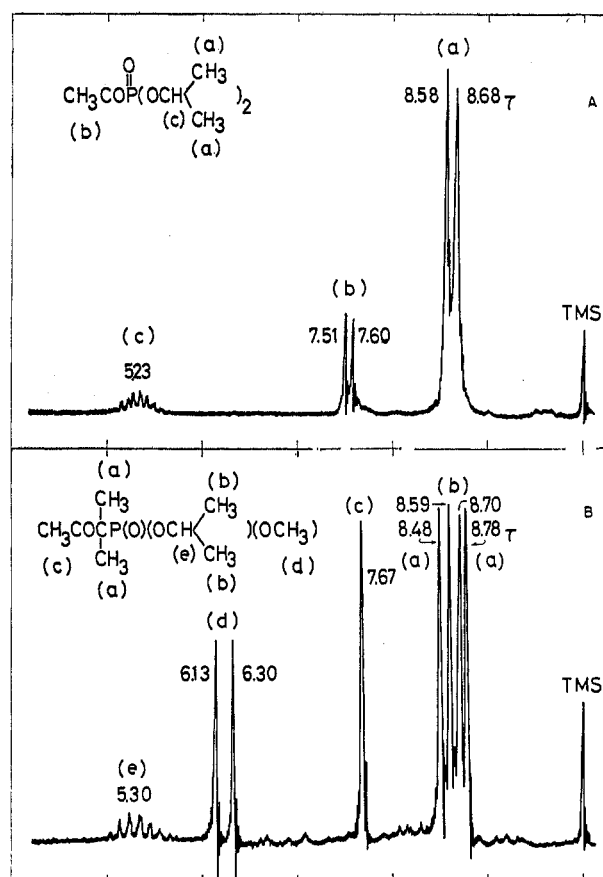


Figure 1.—The nmr spectra of **1c** (A) and **6c** (B) in CCl_4 at room temperature.

$n-\pi^*$ excitation of the carbonyl group of **1** (λ_{max} 335 $m\mu$).

This anomalous photochemical behavior may be related to factors influencing intramolecular hydrogen abstraction and type II elimination. An important factor for photochemical hydrogen abstraction by a carbonyl group is that the lowest triplet state is n,π^* . Electron-releasing groups are known to increase the π,π^* character of the $[n,\pi^*]^3$ state of alkyl phenyl ketones, and thus retard photoreduction.¹⁰ Such effects have been reported¹¹ also in aliphatic α,β -unsaturated ketones, where β -alkyl substituents have a marked effect on the level of the $[\pi,\pi^*]^3$ state. The reverse would, however, be true for α -ketophosphonates in which the electron-attracting phosphoryl group α to the carbonyl may reduce the coupling between the $[n,\pi^*]^3$ state and π,π^* states and enhance the photochemical reactivity of the $[n,\pi^*]^3$ state;¹² thus β -ketophosphonates were found to be photoreduced more efficiently than other simple aliphatic ketones.³

As to the geometrical features, the preferred transition state for intramolecular hydrogen abstraction is that in which the participating carbon, hydrogen, and nonbonding electron on oxygen can approximate a linear configuration.¹³ In the most stable conformation

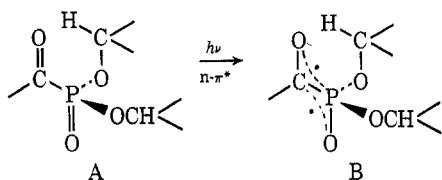
(10) (a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 156. (b) For recent studies in this area, see P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **90**, 5898 (1968); N. C. Yang and R. L. Dusenbery, *ibid.*, **90**, 5899 (1968); J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *ibid.*, **90**, 5902 (1968).

(11) R. B. Woodward, *ibid.*, **63**, 1123 (1941); **64**, 76 (1942).

(12) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *ibid.*, **89**, 5466 (1967).

(13) (a) N. J. Turro and D. W. Weiss, *ibid.*, **90**, 2185 (1968); (b) A. Padwa, E. Alexander, and M. Niemczyk, *ibid.*, **91**, 456 (1969).

(A) of α -ketophosphonates, however, the C=O and P=O dipoles may be pointing in opposite directions with negative oxygen atoms as far as possible, as is true in α -dicarbonyl compounds.¹⁴ The same conformation may be adopted also in an excited state,



since an excited electron would probably be delocalized over the P=O group through the vacant d orbital on the phosphorus¹⁵ as in B, where two odd electrons tend to separate as far as possible, and free rotation around the C—P bond might be more limited than in the ground state because of the double-bond character of C—P. Spectral evidence^{15,16} (intensification and red shift of the carbonyl $n-\pi^*$ band and shift of the carbonyl stretching frequency to longer wavelength compared with corresponding aldehydes) supports the idea of direct interaction of the carbonyl π orbital with the phosphoryl group in acylphosphonates. Hence the linearity required for hydrogen abstraction is difficult to attain with B because of the coplanarity of $\cdot\text{O}=\text{C}-\text{P}-\text{O}\cdot$. Several similar examples of inefficiency in intramolecular photoreductions of ketones¹⁸ and in intramolecular hydrogen abstraction¹⁷ in the dark have been reported.

Similar effects are operative also in type II elimination, which requires the C—P—O—C to be coplanar and arranged for maximum overlap between the developing p orbitals and the p orbitals at radical sites of the intermediary biradical.^{18b,18} Interaction of two alkyl groups may interfere with this coplanarity of the biradical, if hydrogen abstraction occurred, as is known in the photoelimination of alkyl phenyl ketones.¹⁸ A fairly strong P—O single bond (95 kcal/mol),¹⁹ compared with C—O (83 kcal/mol)²⁰ and C—C (84 kcal/mol)²⁰ might also be related to the failure of elimination.

In spite of this unfavorable conformation of the reactant, the formation of product 2 suggests the occurrence of γ -hydrogen abstraction in the photolysis of 1c–1e. Furthermore, the decrease in yield of 2c in isopropyl alcohol, a good hydrogen donor, suggests that $T_1(n, \pi^*)$ is a reactive state for the rearrangement which is competing with intermolecular hydrogen abstraction, although the nature of the reduction products was not established.

The lack of formation of 2 in the irradiation of diphenyl acetylphosphonate (1f) and β -ketophospho-

nate,⁸ both of which have no available γ hydrogen, supports this assumption. The marked increase in the yield of 2 in going from 1a to 1c–1e is attributable to bond energy and also to the steric effect of two bulky alkyl groups in bringing the γ -hydrogen atom closer to the carbonyl oxygen atom. The yield of 2 shows relative reactivities of primary/secondary/tertiary hydrogen to be 0:5:45; these values differ from those obtained in the other reaction,^{10b} e.g., 1:19:60, and suggest that the steric factor is operative. Therefore, 1a, a ketone with little steric interaction, affords a single product 3a via type I cleavage. In contrast, cyclobutyl phenyl ketone, with an unfavorable conformation for internal hydrogen abstraction, was reported to undergo intermolecular abstraction even in benzene.^{13b} The reduction product could not be isolated in the present reaction, but the polymer containing a C—OH bond may be derived from such a reaction.

These results suggest Scheme I for the rearrangement, which involves initial γ -hydrogen abstraction by an excited carbonyl oxygen. Direct abstraction of a γ hydrogen by phosphoryl oxygen, similar to the photoisomerization of 2,2-dimethylthiachroman 1-oxide,²¹ is less probable in view of the geometry of the reactant.

Pathway b, based on the reaction of diazomethane with dialkyl acylphosphonates, which gives dialkyl acetylphosphonates,^{22a} is less probable because of the rapid insertion of carbene (12) into the acidic O—H bond, compared with carbonyl addition,^{22b} and also because formation of a cleavage product 11 or carbene derivative was not observed.

Intermediary formation of pentacovalent 1,2-oxaphosphirane²³ (10) seems to be more probable than that of 9 because of the absence of 9, although 9 seems to be more stable²⁴ under the reaction conditions than 10. However, a pathway via 9 is not completely excluded at present. A three-membered cyclic analog of 10 has been proposed²⁵ in the photorearrangement of N-phenylphenylbenzoyl nitrene to N,N-dibenzoylaniline. Decomposition of 10 to 2 may proceed thermally, since photolysis of the epoxy ketone has been shown²⁶ to involve preferential fission β to the carbonyl group. The reason that the reaction proceeds via 8 is obscure at this moment. Differences in stability and in steric hindrance to cyclization between 7 and 8 may be responsible; interaction of d-sp² bonding in 8 is apparently less sensitive²⁷ to steric factors because of the

(21) R. A. Archer and B. S. Kitchell, *J. Amer. Chem. Soc.*, **88**, 3462 (1966).

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(23) Oxaphosphirane was reported to form in the reaction of triethyl phosphite with diphenylketene: H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 612 (1919).

(24) Compound 9 appears to have no absorption in the uv region of the lamp used (ca. >300 m μ). Even if the energy transfer occurred from 1 to 9, it is hard to think that 9 is too unstable to be detected under the reaction conditions. Four-membered cyclic phosphorus esters similar to 9 have been reported to be stable enough to be distilled: H. G. Henning and M. Morr, *Chem. Ber.*, **101**, 3963 (1968).

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(14) G. S. Hammond, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1960, p 378.

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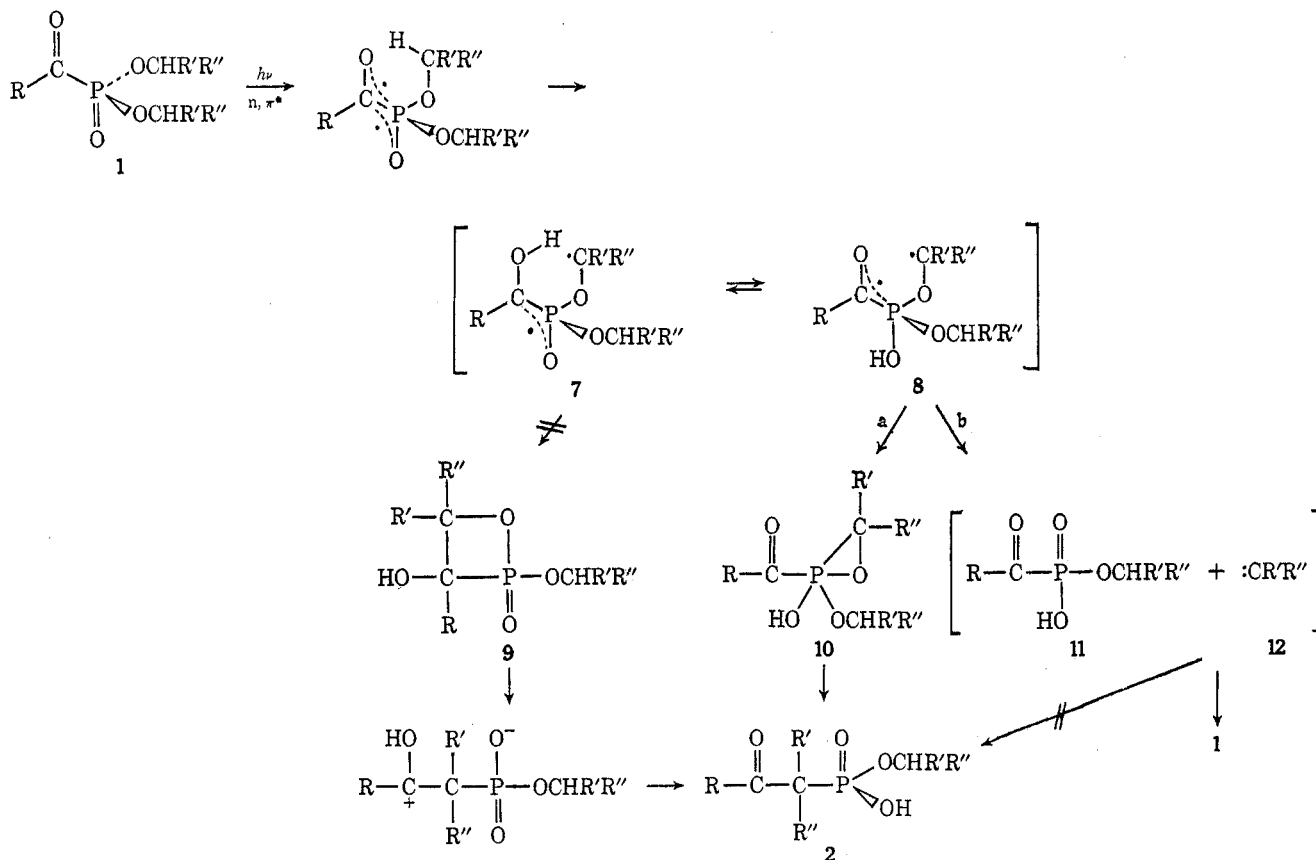
(17) (a) E. J. Corey and W. R. Hertler, *J. Amer. Chem. Soc.*, **82**, 1657 (1960); (b) C. Walling and A. Padwa, *ibid.*, **85**, 1597 (1963).

(18) P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5896 (1968); J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *ibid.*, **90**, 5900 (1968).

(19) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 1201.

(20) See p 824 in ref 2a.

SCHEME I



large number of 3d orbitals. It is hoped that further studies will provide some insight into these problems.

Experimental Section

Melting points and boiling points are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Faculty of Agriculture, Nagoya University, Nagoya, Japan. Instruments used to record spectra were a Shimadzu Type SV-50A (uv), a Perkin-Elmer Model 337 (ir), and a JNM-MH-60 (nmr). Nmr chemical shifts are given in parts per million from TMS (10 in CCl_4 or CDCl_3), J in hertz. Molecular weights were measured in benzene using a Hewlett-Packard vapor pressure osmometer Model 302. A Yanagimoto potentiometric titrator KY-5 type was used for titration. A Yanagimoto Model GCG-500F flame ionization instrument was employed for glpc, using a 2 m \times 3 mm stainless steel column of 5% PEG No. 6000 on 60-80 mesh Celite CS for low boiling products, and a 2 m \times 3 mm stainless steel column of 5% PEG 20M on 60-80 mesh Celite CS for higher boiling materials. Column chromatography was conducted using Mallinckrodt silicic acid (100 mesh), and tlc was accomplished using Merck silica gel G of 250- μ thickness as an absorbent and phosphomolybdic acid as a color reagent.

Materials.—Ketophosphonates (1a–1e, 1g–1h) were prepared by the reaction of corresponding halocarbonyl compounds with trialkyl phosphites²⁸ as described in the literature.²⁹ Diphenyl acetylphosphonate (1f) was prepared by the reaction of acetyl chloride with diphenyl methyl phosphite, bp 167–168° (12 mm), lit.³⁰ bp 165–166.5° (12 mm). Ketophosphinates (1i, 1j) were prepared by the reaction of corresponding halocarbonyl compounds with diisopropyl butylphosphonite, bp 85–87° (18 mm).³¹ Ketophosphine oxide (1k) was prepared from acetyl chloride and ethyl

dibutylphosphinite, bp 85–90° (12 mm), lit.³² bp 88–92° (12 mm). All compounds were purified by reduced pressure distillation and their purity was assessed by tlc and/or glpc. Table II lists their boiling points and ir spectra.

TABLE II
BOILING POINTS AND INFRARED SPECTRA OF
KETOPHOSPHORUS COMPOUNDS

No.	Compd	Bp, °C (mm)	—Ir, cm^{-1} —		
			C=O	P=O	P—O—C
1a	$\text{CH}_3\text{COP}(\text{O})(\text{OMe})_2$	72 (6)	1700	1255	1930
1b	$\text{CH}_3\text{COP}(\text{O})(\text{OEt})_2$	78–80 (4)	1705	1250	1050
1c	$\text{CH}_3\text{COP}(\text{O})(\text{OPr-}i)_2$	73–74 (4)	1710	1258	995
1d	$\text{CH}_3\text{COP}(\text{O})(\text{OBu-}sec)_2$	101–102 (5)	1700	1258	990
1e	$\text{PhCOP}(\text{O})(\text{OPr-}i)_2$	147–149 (5)	1650	1250	996
1f	$\text{CH}_3\text{COP}(\text{O})(\text{OPh})_2$	165–167 (1.5)	1760	1280	1015
1g	$\text{EtOCCP}(\text{O})(\text{OEt})_2$	133 (12.5)	1710	1270	1015
1h	$\text{EtOCCP}(\text{O})(\text{OPr-}i)_2$	117–118 (9)	1715	1270	996
1i	$\text{CH}_3\text{COP}(\text{O})(\text{OPr-}i)(\text{Bu})$	101–103 (6)	1697	1235	980
1j	$\text{CH}_3\text{COCH}_2\text{P}(\text{O})(\text{OPr-}i)(\text{Bu})$	115–116 (5)	1705	1235	983
1k	$\text{CH}_3\text{COP}(\text{O})(\text{Bu})_2$	129 (2.5)	1710	1160	

A General Procedure for Irradiation.—A solution of ketophosphorus compounds (0.01 mole) in benzene (100 ml) was placed in a quartz or Pyrex well equipped with a N_2 inlet tube, a thermometer and a water-cooled condenser. For the reactions in which low-boiling products such as 1-butene are expected, an outlet tube connected to the condenser leads to a Dry Ice cooled trap. A high-pressure Halos 400-W Hg lamp with a water-cooled quartz jacket was used as an external light source. The reaction vessel and light source were immersed in a water bath. N_2 gas was passed through the solution before and during the irradiation. The progress of the reaction was monitored by removing aliquots with a syringe and examination by tlc and glpc. No component with a shorter retention time than benzene itself was found.

Irradiation of 1c.—A solution of 2.0 g (0.0095 mol) of 1c in benzene (100 ml) was irradiated until no 1c was detected by tlc (ca. 4 hr). The ir spectrum (CHCl_3) of the product had strong absorptions at ~ 2700 and 2250 (P—OH), and 1710 cm^{-1} (C=O).

(28) A. H. Ford-Moore and B. J. Perry "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 955.

(29) M. I. Kabachnik and P. A. Rossičskaya, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 364 (1945); *Chem. Abstr.*, **40**, 4688 (1946).

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(32) M. Sander, *Chem. Ber.*, **93**, 1220 (1960).

The carbonyl absorption did not disappear after refluxing the irradiated mixture in an alkaline or acid aqueous solution, although **1c** was easily hydrolyzed to give acetic acid and diisopropyl hydrogen phosphonate. Potentiometric titration showed that the product contained 90.8% acid.

Addition of cyclohexylamine (2.0 g, 0.02 mol) to the product gave crude **5c** (needles from dioxane): 2.15 g (72.5%); mp 156–157°; ir (KBr disk), 2950, 1640, 1550 ($-\text{NH}_3^+$), and 1710 cm^{-1} ($\text{C}=\text{O}$).

Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_4\text{P}$: C, 54.70; H, 9.84; N, 4.56; neut equiv, 307. Found: C, 54.86; H, 9.63; N, 4.53; neut equiv, 305.

The product acid was dissolved in ethyl ether (20 ml) and a freshly prepared³³ ethereal solution of diazomethane was added dropwise with stirring at 5° until N_2 evolution ceased. The solution was allowed to stand overnight. After evaporation of ether, the reaction mixture was chromatographed on a 2.1×50 cm silica gel column slurry packed in 10% acetone in benzene. Increasing amounts of acetone were used. Analysis of the eluate was conducted by tlc using benzene–acetone (4:1) as solvent. The first fraction of R_f 0.81 was diisopropyl phenylphosphonate (**3c**, 0.058 g, 2.5%): ir (film), 3050, 1600, 1470 ($-\text{Ph}$), 1450 ($\text{Ph}-\text{P}$), 1248 ($\text{P}=\text{O}$), 995 ($\text{P}-\text{O}-\text{C}$), 740 and 690 cm^{-1} (five adjacent 5 H); nmr (CCl_4), τ 2.23–2.55 (5 H, m, C_6H_5), 5.39 (2 H, d, $J_{\text{HP}} = 1.5$, of septets, $J_{\text{HH}} = 6.0$, $\text{P}-\text{O}-\text{CH}$), and 5.63 [12 H, d, $J = 6.0$, $\text{CH}(\text{CH}_3)_2$]. The second main fraction of R_f 0.70 was isopropyl methyl β -ketophosphonate (**6c**, 1.789 g, 83.5%): ir (film), 1710 ($\text{C}=\text{O}$), 1350 (CH_3CO), 1248 ($\text{P}=\text{O}$), 1040, and 990 cm^{-1} ($\text{P}-\text{O}-\text{C}$); nmr (CCl_4), τ 5.30 (1 H, d, $J_{\text{HP}} = 1.5$, of septets, $J_{\text{HH}} = 6.0$, $\text{P}-\text{O}-\text{CH}$), 6.22 (3 H, d, $J_{\text{HP}} = 10.5$, $\text{P}-\text{O}-\text{CH}_3$), 7.67 (3 H, s, COCH_3), 8.63 [6 H, d, $J_{\text{HH}} = 6.0$, $-\text{CH}(\text{CH}_3)_2$], and 8.65 [6 H, d, $J_{\text{HH}} = 18.0$, $\text{P}-\text{C}(\text{CH}_3)_2$].

Anal. Calcd for $\text{C}_8\text{H}_{17}\text{O}_4\text{P}$: mol wt, 222. Found: mol wt, 211.

The last fraction of R_f 0.10 was a hygroscopic viscous liquid which has a broad ir and nmr spectra (**4c**, 0.206 g, 10.3 wt %): ir (film), ~ 3380 ($\text{C}-\text{OH}$), 1710 ($\text{C}=\text{O}$), 1225 ($\text{P}=\text{O}$), and 990 ($\text{P}-\text{O}-\text{C}$) cm^{-1} ; nmr (CDCl_3), τ 5.23 (m, $\text{P}-\text{O}-\text{CH}$), 5.72 (broad s, $\text{C}-\text{OH}$), 7.66 (s, CH_3CO), and 8.70 (m).

Attempted distillation of the main product gave a rather poor yield of **6c** because of decomposition during distillation; thus a solution of 6.1 g (0.027 mol) of **1c** in benzene (500 ml) was irradiated and the irradiated mixture distilled after treatment with diazomethane. A fraction boiling at 85–90° (3 mm) was identified as **6c** by tlc and nmr and collected (1.68 g, 28%). A considerable amount of low-boiling fraction and residue was also collected, which might be decomposition products.

Irradiation of 1d.—A solution of 2.4 g (0.01 mol) of **1d** in benzene (100 ml) was irradiated and worked up as described above. Cyclohexylammonium salt (**5d**, 2.18 g, 63.7%): mp 161–162° (from dioxane–acetonitrile); ir (KBr disk), 2950, 2500 ($-\text{NH}_3^+$), 1710 ($\text{C}=\text{O}$), and 1248 cm^{-1} ($\text{P}=\text{O}$).

Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_4\text{P}$: C, 57.29; H, 10.22; N, 4.18; neut equiv, 335. Found: C, 57.13; H, 10.19; N, 4.30; neut equiv, 332.

Chromatographic separation of products after treatment with diazomethane gave the following products. **3d** (R_f 0.82, 0.11 g, 4%): ir (film), 3050, 1602, 1460 ($-\text{Ph}$), 1450 ($\text{Ph}-\text{P}$), 1250 ($\text{P}=\text{O}$), 990 ($\text{P}-\text{O}-\text{C}$), 750, and 695 cm^{-1} (adjacent 5 H); nmr (CCl_4), τ 2.52–2.73 (5 H, m, C_6H_5), 5.57 (2 H, d, $J_{\text{HP}} = 1.5$, of sextets, $J_{\text{HH}} = 6.0$, $\text{P}-\text{O}-\text{CH}$), 8.63 (4 H, quintet, $J_{\text{HH}} = 6.8$, $\text{CH}-\text{CH}_2-\text{CH}_3$), 8.68 (6 H, d, $J_{\text{HH}} = 6.0$, $\text{CH}-\text{CH}_3$), and 9.06 (6 H, t, $J_{\text{HH}} = 6.8$, CH_2-CH_3). **6d** (R_f 0.73, 1.85 g, 72.6%): ir (film), 1705 ($\text{C}=\text{O}$), 1350 (CH_3CO), 1250 ($\text{P}=\text{O}$),

1040, and 995 cm^{-1} ($\text{P}-\text{O}-\text{C}$); nmr (CCl_4), τ 5.55 (1 H, d, $J_{\text{HP}} = 1.5$, of sextets, $J_{\text{HH}} = 6.0$, $\text{P}-\text{O}-\text{CH}$), 6.37 (3 H, d, $J_{\text{HP}} = 10.5$, $\text{P}-\text{O}-\text{CH}_3$), 7.70 (3 H, s, CH_3CO), 8.17–8.55 (4 H, m, $\text{CH}-\text{CH}_2-\text{CH}_3$ and $\text{P}-\text{C}-\text{CH}_2-\text{CH}_3$), 8.71 (3 H, d, $J_{\text{HH}} = 6.0$, $\text{O}-\text{CH}-\text{CH}_3$), and 9.06 (3 H, t, $J_{\text{HH}} = 6.8$, CH_2-CH_3). **4d** (R_f 0.13, 0.573 g, 22.7 wt %): ir (film), ~ 3350 ($\text{C}-\text{OH}$), 1700 ($\text{C}=\text{O}$), 1215 ($\text{P}=\text{O}$), and 1025 cm^{-1} ($\text{P}-\text{O}-\text{C}$).

Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{O}_4\text{P}$ (**6d**): mol wt, 250. Found: mol wt, 242.

Irradiation of 1b.—Irradiation of **1b** (1.8 g, 0.01 mol) in benzene (100 ml) gave the following results. Cyclohexylammonium salt (**5b**, 0.28 g, 10%): mp 151–152° (from dioxane); ir (KBr disk), 2950, 2500 ($-\text{NH}_3^+$), 1700 ($\text{C}=\text{O}$), and 1250 cm^{-1} ($\text{P}=\text{O}$).

Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{NO}_4\text{P}$: C, 51.60; H, 9.38; N, 5.01; neut equiv, 279. Found: C, 51.63; H, 9.42; N, 4.98; neut equiv, 282.

Chromatographic separation of the mixture after treatment with diazomethane gave the following products. **3b** (R_f 0.83, 0.135 g, 6.3%): ir (film), 3060, 1603, 1465 ($-\text{Ph}$), 1450 ($\text{Ph}-\text{P}$), 1248 ($\text{P}=\text{O}$), 1010 ($\text{P}-\text{O}-\text{C}$), 758, and 695 cm^{-1} (adjacent 5 H); nmr (CCl_4), τ 2.50–2.72 (5 H, m, C_6H_5), 5.99 (4 H, d, $J_{\text{HP}} = 1.5$, of quartets, $J_{\text{HH}} = 6.8$, $\text{P}-\text{O}-\text{CH}_2$), and 8.64 (6 H, t, $J_{\text{HH}} = 6.4$, $\text{P}-\text{O}-\text{CH}_2-\text{CH}_3$). **6b** (R_f 0.72, 0.241 g, 12.4%): ir (film), 1710 ($\text{C}=\text{O}$), 1350 (CH_3CO), 1248 ($\text{P}=\text{O}$), and 1030 cm^{-1} ($\text{P}-\text{O}-\text{C}$); nmr (CCl_4), τ 6.02 (2 H, d, $J_{\text{HP}} = 1.5$, of quartets, $J_{\text{HH}} = 6.8$, $\text{P}-\text{O}-\text{CH}_2$), 6.19 (3 H, d, $J_{\text{HP}} = 10.5$, $\text{P}-\text{O}-\text{CH}_3$), 7.83 (3 H, s, CH_3CO), 8.50–8.82 (3 H, m, $\text{P}-\text{CH}-\text{CH}_3$), and 8.74 (3 H, t, $J_{\text{HH}} = 6.4$, $\text{P}-\text{O}-\text{CH}_2-\text{CH}_3$). **4b** (R_f 0.15, 1.310 g, 72.8 wt %): ir (film), ~ 3380 ($\text{C}-\text{OH}$), 1700 ($\text{C}=\text{O}$), 1210 ($\text{P}=\text{O}$), and 1020 ($\text{P}-\text{O}-\text{C}$); nmr (CDCl_3), τ 5.62 (broad s, $\text{C}-\text{OH}$), 6.12 (m), 7.90 (s, CH_3CO), and 8.70 (m).

Irradiation of 1e.—Irradiation of **1e** (2.7 g, 0.01 mol) in benzene (100 ml) gave white needles (**2e**, 2.03 g, 75%) on standing in a refrigerator for about 1 week: mp 79–80°; ir (KBr disk), 3060, 1590, 1440 ($-\text{Ph}$), 2700, 2280 ($\text{P}-\text{OH}$), 1660 ($\text{C}=\text{O}$), 1250 ($\text{P}=\text{O}$), 995 ($\text{P}-\text{O}-\text{C}$), 759, and 704 cm^{-1} (adjacent 5 H); nmr (CCl_4), τ 2.05–2.57 (5 H, m, C_6H_5), 5.38 (1 H, d, $J_{\text{HP}} = 1.5$, of septets, $J = 6.0$, $\text{P}-\text{O}-\text{CH}$), 8.67 [6 H, d, $J_{\text{HH}} = 6.8$, $\text{CH}(\text{CH}_3)_2$], and 8.61 [6 H, d, $J_{\text{HP}} = 15.5$, $\text{P}-\text{C}(\text{CH}_3)_2$].

Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{O}_4\text{P}$: C, 57.77; H, 7.09; neut equiv, 270. Found: C, 57.70; H, 7.05; neut equiv, 268.

Irradiation of 1a.—An irradiated mixture of **1a** (1.52 g, 0.01 mol) gave no ammonium salt on addition of amine. Further, dimethyl acetylphosphonate (**6a**) could not be detected by glpc after treatment with diazomethane. Chromatographic separation of the mixture gave the following products. **3a** (R_f 0.78, 0.46 g, 24.6%): ir (film), 3060, 1600, 1460 ($-\text{Ph}$), 1450 ($\text{Ph}-\text{P}$), 1240 ($\text{P}=\text{O}$), 1025 ($\text{P}-\text{O}-\text{C}$), 750, and 695 cm^{-1} (adjacent 5 H); nmr (CCl_4), τ 2.25–2.59 (5 H, m, C_6H_5) and 6.38 (6 H, d, $J_{\text{HP}} = 10.5$, $\text{P}-\text{O}-\text{CH}_3$). **4a** (R_f 0.12, 1.028 g, 67.6 wt %): ir (film), 3400–3300 ($\text{C}-\text{OH}$), 1700 ($\text{C}=\text{O}$), 1215 ($\text{P}=\text{O}$), and 1025 cm^{-1} ($\text{P}-\text{O}-\text{C}$); nmr (CDCl_3), τ 4.87 (broad s, $\text{C}-\text{OH}$), 6.31 (d, $\text{P}-\text{O}-\text{CH}_3$), and 7.90 [s, CH_3CO or $\text{CH}_3\text{C}(\text{OH})$].

Registry No.—**1a**, 17674-28-1; **1b**, 919-19-7; **1c**, 20526-22-1; **1d**, 22950-56-7; **1e**, 22950-57-8; **1f**, 22950-58-9; **1g**, 1474-78-8; **1h**, 22950-60-3; **1i**, 22950-61-4; **1j**, 22950-62-5; **1k**, 14313-75-8; **2e**, 22950-64-7; **3a**, 2240-41-7; **3b**, 1754-49-0; **3c**, 7237-16-3; **3d**, 2783-48-4; **5b**, 22950-69-2; **5c**, 22950-70-5; **5d**, 22950-71-6; **6b**, 22950-72-7; **6c**, 22950-73-8; **6d**, 22950-74-9.

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