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THE PHOTOCHEMICAL REACTIONS OF SUBSTITUTED ACETONES WITH TRIETHYL PHOSPHITE[1]

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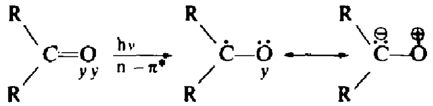
Abstract—Photochemical reactions of substituted acetones with triethyl phosphite have been studied to investigate the chemical behaviour of the n–π* excited state of the CO group. UV irradiation of an ethereal solution of chloroacetone (Ia) and triethyl phosphite (II) at 20° gives vinyl phosphate (III) and ketophosphonate (IV), together with other by-products. The yield of IV decreases by addition of a radical scavenger, hydroquinone, whereas the yield of III is little affected. Addition of methanol and acetic acid suppresses the reaction. A similar reaction is possible with other substituted acetones. The ratio of [III]/[IV] varies with derivatives of acetones. A probable mechanism is discussed.

It is well known that ketones and aldehydes are excited on absorption of 260–300 mμ light to afford an n–π* excited state which may be written as a resonance hybrid as follows:



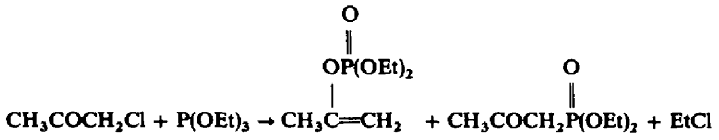
One of the characteristic feature of the n–π* excited state is a negative formal charge on the carbon and a positive formal charge on the oxygen which is the reversal of ordinary carbonyl π-electron polarization.

Since little information is available on the application of this n–π* excited state to organic syntheses, photochemical reactions of substituted acetones with triethyl phosphite giving vinyl phosphate (Perkow reaction) and ketophosphonate (Arbuzov reaction)[3] have been investigated. The photoinduced Arbuzov reaction, e.g. the photolysis of trialkyl phosphites alone to yield dialkyl alkylphosphonates[4] and a similar photolysis in the presence of phenyl iodide to yield dialkyl phenylphosphonates[5] have been reported, but no mechanism has been offered for the photo-induced Perkow reaction.

Data is now presented which indicate that the Perkow reaction is accelerated and/or initiated by irradiation of UV light under conditions where no dark reaction is appreciable.

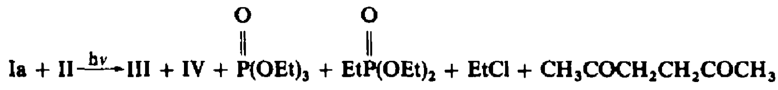
RESULTS AND DISCUSSION

Chloroacetone (Ia) reacts with triethyl phosphite (II) above 110°, yielding vinyl phosphate (III) and ketophosphonate (IV), but at room temperature if the concentration of reactants in solution is low, the reaction only proceeds with difficulty. UV irradiation of an ethereal solution of chloroacetone ($\lambda_{max}^{Et_2O}$, 290 mμ) and triethyl



$$\underset{\text{Ia}}{CH_3COCH_2Cl} + \underset{\text{II}}{P(OEt)_3} \rightarrow \underset{\text{III}}{CH_3\overset{\overset{\overset{O}{\|}}{OP(OEt)_2}}{\overset{|}{C}}{=}CH_2} + \underset{\text{IV}}{CH_3COCH_2\overset{\overset{O}{\|}}{P}(OEt)_2} + EtCl$$

phosphite in a quartz vessel with an unfiltered high-pressure mercury lamp at 20° yields III and IV, together with triethyl phosphate (V), diethyl ethylphosphonate (VI), ethyl chloride and biacetonyl (VII).



$$\text{Ia} + \text{II} \xrightarrow{h\nu} \text{III} + \text{IV} + \underset{\text{V}}{\overset{\overset{O}{\|}}{P}(OEt)_3} + \underset{\text{VI}}{Et\overset{\overset{O}{\|}}{P}(OEt)_2} + EtCl + \underset{\text{VII}}{CH_3COCH_2CH_2COCH_3}$$

Analysis and estimation of the products were performed by GLC, TLC and IR spectroscopy. The formation of III and IV is also observed in a Pyrex reaction tube, but no detectable reaction takes place without UV light under these conditions and with similar work-up.

Addition of hydroquinone as a radical scavenger to the reaction decreases the yield of IV, whereas the yield of III is little affected (Table 1). This result, together with the formation of biacetonyl (VII), suggests the radical nature of the reaction for the formation of IV, i.e. photo-induced Arbuzov reactions.[5, 6] The attack of the acetonyl radical derived from the C—Cl bond fission of Ia on the trivalent P atom yields the phosphoranyl radical (VIII) followed by the one-electron transfer from VIII to a Cl atom to yield the keto quasiphosphonium salt (IX) which collapses to give ketophosphonate (IV) and ethyl chloride.

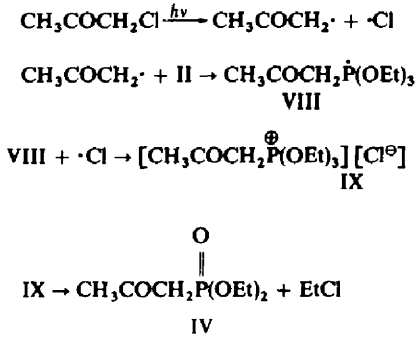
TABLE 1. THE EFFECTS OF ADDED SPECIES ON THE YIELDS OF III AND IV[a]

Added species	Concentration M	Yields[b], % III	Yields[b], % IV
None	—	6·6	17·4
Hydroquinone	0·00126	5·9	16·1
	0·00268	6·1	15·1
	0·0124	5·3	7·0
	0·0222	4·9	4·3
	0·0596	4·2	0
Acetic acid	0·350	4·8	13·5
	0·700	3·8	10·5
Methanol[c]	—	2·0	6·2

[a] Irradiation of ethereal solution of chloroacetone (0·12M) and triethyl phosphite (0·06M) for 1 hr.

[b] Based on triethyl phosphite used.

[c] Solvent.



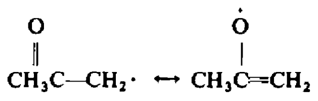
$$CH_3COCH_2Cl \xrightarrow{h\nu} CH_3COCH_2\cdot + \cdot Cl$$

$$CH_3COCH_2\cdot + II \rightarrow \underset{VIII}{CH_3COCH_2\dot{P}(OEt)_3}$$

$$VIII + \cdot Cl \rightarrow \underset{IX}{[CH_3COCH_2\overset{\oplus}{P}(OEt)_3][Cl^{\ominus}]}$$

$$IX \rightarrow \underset{IV}{CH_3COCH_2\overset{O}{\overset{\|}{P}}(OEt)_2} + EtCl$$

The formation of the acetonyl radical in the photolysis of Ia with light of wave length 313 mμ has already been shown. Although two canonical forms may be described for the acetonyl radical (Xa and Xb), a product derived from Xb has not been reported;



$$\underset{Xa}{CH_3\overset{O}{\overset{\|}{C}}-CH_2\cdot} \leftrightarrow \underset{Xb}{CH_3\overset{\dot{O}}{\overset{|}{C}}=CH_2}$$

hence, the formation of vinyl phosphate (III) by a radical reaction of Xb with II seems unreasonable.

Consequently, similar photochemical reactions with acetones CH_3COCH_2Y (Ib–f) having a α-substituent as a leaving group were investigated in order to elucidate the mechanism of the photo-induced Perkow reaction. The results are shown in Table 2. The ratio of [III]/[IV] varies according to the substituent, although a similar ratio is expected if III and IV are derived from the same radical species. In the reaction of triethyl phosphite with acetoxyacetone (Ib), in which the acetoxy group is known to depart readily as an acetate ion, the formation of III is favoured. Whereas, smaller amounts of III and IV were detected in reactions with substituted

TABLE 2. THE PHOTOCHEMICAL REACTIONS OF SUBSTITUTED ACETONES WITH TRIETHYL PHOSPHITE[a]

Y in CH_3COCH_2Y	$\lambda_{max}^{Et_2O}$ mμ	Time hr	Yields[b], %	
			III	IV
Ia, Cl	290·0	4	5·3 (7·2)	19·0
a, Cl[c]		4	3·0 (5·9)	12·0
b, OAc[d]	274·5	20	22·0	3·0 (6·8)
c, OEt	288·0	20	1·5	2·7
d, OMe	286·5	20	1·0	2·5
e, OH	261·5	20	1	2·0
f, H[e]	267·0	20	0	2·0

[a] Irradiation of ethereal solution of I (0·12M) and II (0·06M).

[b] Based on II used. Parenthesized numbers are maximum yields (see Fig. 1).

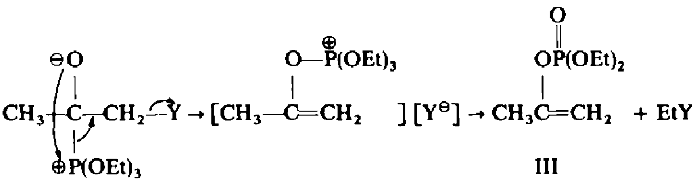
[c] In Pyrex tube.

[d] Ethyl acetate was detected.

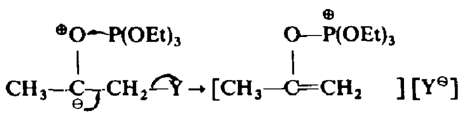
[e] Acetone was used as solvent.

acetones (Ic, d, e and f), the substituent in each compound is less able to leave as an anion or a radical than chlorine or the acetoxy group.[8] These results, coupled with the fact that the yield of III is little affected by a radical scavenger, suggest an ionic nature of the reaction to form III. However, a smaller amount of III is detected in the reaction with Ia than with Ib, although the substituent of Ia departs more readily as chlorine than that of Ib.[9] This may be explained by assuming that Ia is more susceptible to homolytic fission than Ib because of the lower bond dissociation energy of C—Cl in Ia (C—Cl, 78 kcal/mole[10]) than C—OAc in Ib (C—OAc, 86 kcal/mole[10]). However, the situation is more complicated by the fact that the rate of photolysis of III is accelerated in the presence of Ia as stated later.

The Perkow reaction in the dark may involve an initial nucleophilic attack of the P atom on a carbonyl C atom followed by the rearrangement to an O atom to form an enol quasiphosphonium salt which is accelerated by acetic acid.[11] The effect of added acetic acid was explained by the protonation of carbonyl, increasing the electrophilicity of carbonyl carbon. On the contrary, in the present reaction, protic solvents such as methanol and acetic acid, in which n–π* excitation is inhibited by their hydrogen-bonding with non-bonding electron on oxygen, retarded the photochemical reaction (Tables 1 and 2). This, together with the fact that the formation of III and IV was observed in the reaction in a Pyrex tube, suggested that the primary process of this reaction is n–π* excitation of the carbonyl group. Therefore, the reaction to form III under irradiation may involve an initial nucleophilic attack of phosphorus on carbonyl oxygen to form an enol quasi-phosphonium salt. The π-electron polarization



$$CH_3-\overset{\ominus O}{\underset{\oplus P(OEt)_3}{C}}-CH_2-Y \rightarrow [CH_3-\overset{O-\overset{\oplus}{P}(OEt)_3}{C}=CH_2][Y^{\ominus}] \rightarrow \underset{\text{III}}{CH_3\overset{OP(O)(OEt)_2}{C}=CH_2} + EtY$$



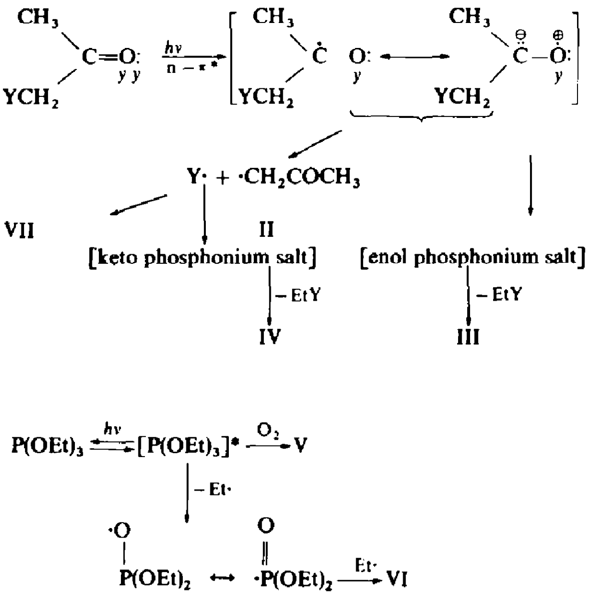
$$CH_3-\underset{\ominus}{\overset{\oplus O-P(OEt)_3}{C}}-CH_2-Y \rightarrow [CH_3-\overset{O-\overset{\oplus}{P}(OEt)_3}{C}=CH_2][Y^{\ominus}]$$

of carbonyl in the n–π* excited state may facilitate the attack of phosphorus on oxygen and the incident negative charge on carbonyl carbon may bring about an anionic expulsion of the substituent.

Fig. 1 shows the correlation of the yields of III and IV with irradiation time for the reactions with Ia and Ib. Both III and IV showed a maximum in their yields. Compounds III ($\lambda_{max}^{Et_2O}$ 259 mμ) and IV ($\lambda_{max}^{Et_2O}$ 276 mμ), are stable in the dark even at 170° and can be photolysed under very prolonged irradiation (Fig. 2). The rate of photolysis of III is greatly accelerated by the presence of Ia, while that of IV is little affected. This phenomena may be explained by the decomposition and/or polymerization of III induced by Ia under irradiation, although GLC identification of the decomposition products failed. GLC analysis of the product in the photolysis of IV shows no formation of III, although rearrangement of ketophosphonate to vinyl phosphate have been reported to occur in the dark in the presence of protonating agents such as acetic[11] or phosphoric acid.[12]

The pathway for the reaction leading to other by-products has been proposed by several authors, i.e. the photo-oxidation[13] of II with dissolved oxygen to yield triethyl phosphate (V) and the photo-induced intramolecular Arbuzov reaction[4] to yield diethyl ethylphosphonate (VI). The reaction mechanism is summarized in Scheme 1.

Scheme 1



EXPERIMENTAL

The IR spectra were obtained as liquid film on Perkin–Elmer Model 337 grating instruments and UV spectra were recorded by Shimadzu type SV-50A. Yanagimoto Model GCG-220 was used for GLC and Merck silica gel G was used for TLC.

Solvents. Ethyl ether was dried over Na metal and distilled. MeOH was also distilled over CaO.

Reagents. Triethyl phosphite (II) was prepared[14] by the reaction of PCl_3 with abs EtOH in the presence of N,N-diethylaniline, dried over Na metal, b.p. 57–58° (19mm) [lit.[15] b.p. 57·5° (19mm)]. Acetoxyacetone (Ib) was prepared[16] by the reaction of bromoacetone with dry AcOK in abs EtOH, b.p. 174–175° (lit.[17] b.p. 170–174°). Ethoxyacetone (Ic) was obtained by Grignard reaction[18] of MeMgI with ethoxyacetonitrile, prepared[19] by cyanation of chloromethyl ethyl ether,[20] b.p. 35° (28 mm) [lit.[18] b.p. 34–36° (28 mm)]. Methoxyacetone (Id) was prepared[21] by the oxidation of 1-methoxypropanol obtained from the reaction[22] of propylene oxide with MeOH and Na, b.p. 114–115° (lit.[21] b.p. 1145–115·0°). Hydroxyacetone (Ie) was prepared[23] by the reaction of bromoacetone with HCOOEt, MeOH and KOH, b.p. 49–51° (20 mm) [lit.[23] b.p. 40–43° (12 mm)]. Other reagents were purchased from Tokyo Kasei Organic Chemicals Co. and purified unless otherwise stated. All reagents were distilled immediately prior to use in irradiation experiments.

Authentic materials. Compounds III (b.p. 96–98° (12 mm), lit.[24] b.p. 97–98° (12 mm)] and IV [b.p. 97–98° (1·5 mm), lit.[24] b.p. 97–98° (1·5 mm)] were prepared[24] by the reaction of bromoacetone with II at 160° and purified by duplicate rectifications. IR bands of III showed no C=O stretching and appeared at 3110,

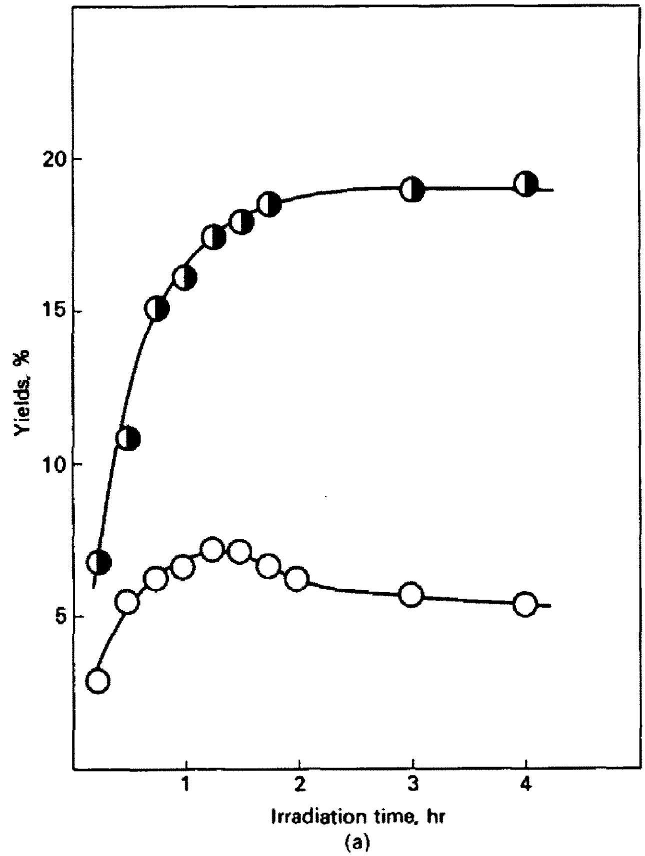
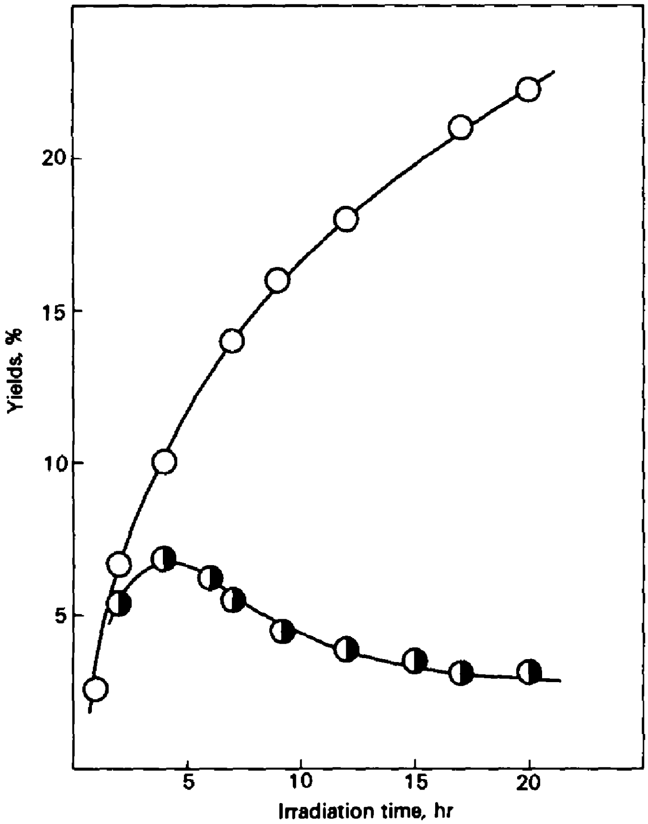


FIG. 1 The correlation curves of the yields of III (—○—) and IV (—◑—) with irradiation time in the reaction of triethyl phosphite with chloroacetone (a) and acetoxyacetone (b) at 20° in a quartz vessel.



(b)

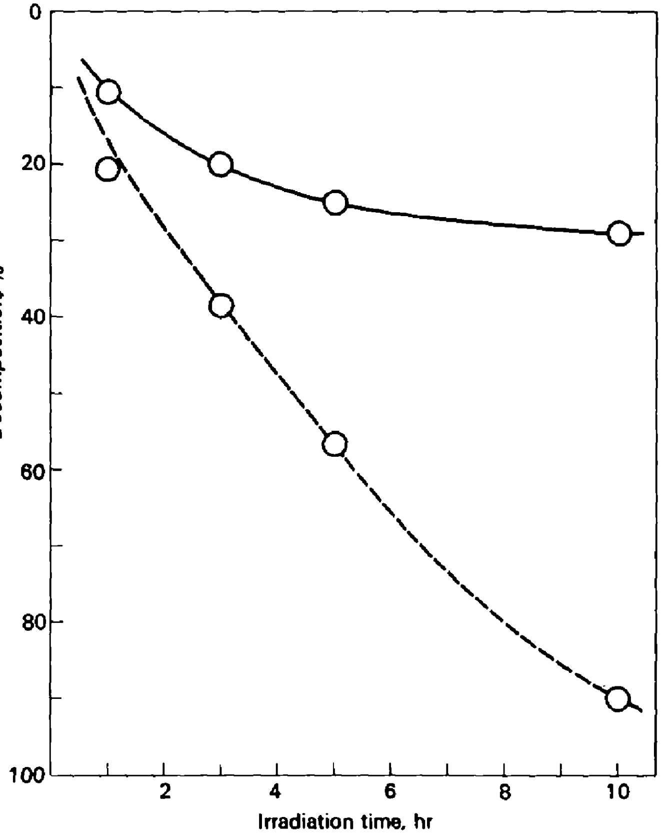


FIG. 2. The photodecomposition of ethereal solution of III without added species (solid line) and in the presence of chloroacetone (broken line). Initial concentration: [III] = 0·01M, [Ia] = 0·12M.

1660 and 906 ($C{=}CH_2$), 1275 ($P{=}O$) and 1165 cm^{-1} (P—O—Et), whereas IR bands of IV appeared at 1725 ($C{=}O$), 1260 ($P{=}O$) and 1165 cm^{-1} (P—O—Et) and no bands corresponding to $C{=}C$ was observed. Compound V was prepared[25] by the reaction of $POCl_3$ with EtONa in EtOH, b.p. 105–106° (15 mm) [lit.[26] b.p. 99·2° (13 mm)]. Its IR bands appeared at 1263 ($P{=}O$) and 1178 cm^{-1} (P—O—Et). Compound VI was prepared[27] by Arbuzov reaction of II with EtI, b.p. 96–97° (25 mm) [lit.[27] b.p. 90–92° (16 mm)]. Its IR bands appeared at 1250 ($P{=}O$) and 1163 cm^{-1} (P—O—Et). Other authentic materials were purchased from Tokyo Kasei Organic Chemicals Co. and purified. The purity of all authentic materials was assesed by GLC and a single peak was observed for each authentic material.

Irradiation experiments. A soln of 0·12M acetone and 0·06M triethyl phosphite in ethyl ether (100 ml) was placed in a quartz or Pyrex tube equipped with a N_2 inlet tube, a thermometer and a water-cooled condenser. A high-pressure Halos 400 W Hg lamp with a water-cooled quartz jacket was used as a light source. The reaction vessel and light source were immersed in a water-bath. N_2 was passed through the soln before and during the irradiation for the agitation and the prevention of oxidation of II. After completing the irradiation, ether was removed under reduced press and the residual liquid was immediately analysed by GLC, TLC and IR spectroscopy.

Irradiation in the presence of added species was performed as follows: I and II were added to an ethereal soln (100 ml) of the added species (hydroquinone or acetic acid) and placed in a quartz vessel, which was irradiated together with another vessel containing an ethereal soln of I and II for comparison.

Identification and estimation of products. GLC analysis was carried out using the following columns and conditions: (a) 2 m column of 25% Silicone DC 550 on 40–60 mesh Celite 545 at 120° using He as a carrier gas (50 ml/min). (b) 2 m column of 20% PEG 20M on 60–80 mesh Celite 545 at 150° using He as a carrier gas (40 ml/min). All peaks were identified by "spiking" with an authentic sample of the given material. Quantitative analyses were performed using condition (a) by addition of a known weight of a standard material (ethyl phenylacetate) to the sample and a comparison of the areas of the peaks produced with those of a mixture of known weights of the compounds and the standard. The reproducibility and reliability of a calibration curve was checked using a standard soln before and after analysis, since vinyl phosphate is unstable under these conditions.

For the confirmation of the reaction products, the IR spectrum of the reaction mixture, after completing the irradiation, was taken, showing absorption at 1725 cm^{-1} ($C=O$) and 3110, 1660 and 906 cm^{-1} ($C=C$).

A mixture of acetone–benzene (1 : 3) was used as developing solvent for TLC. After being developed, the chromatoplate was sprayed successively with 2% 2,6-dichloroquinone-4-chlorimide-ethanol and 2% borax-water.[28] The similarities between colours (blue) and R_f values (0·38 for III and 0·18 for IV) for the sample and authentic materials established their identities.

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REFERENCES

[1] Contribution No. 112.
[2] J. Sidman, *Chem. Rev.* **58**, 689 (1958); H. E. Zimmerman, *Advances in Photochemistry* (Edited by W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr.) Vol. 1; p. 183. Wiley, New York (1963).
[3] For general reviews, see F. W. Lichtenthaler, *Chem. Rev.* **61**, 607 (1961); B. Miller, *Topics in Phosphorus Chemistry* (Edited by M. Grayson and E. J. Griffith) Vol. 2; p. 175. Wiley, New York (1965).
[4] R. B. Lacount and C. E. Griffin, *Tetrahedron Letters* 3071 (1965).
[5] J. B. Plumb, R. Obrÿcki and C. E. Griffin, *J. Org. Chem.* **31**, 2455 (1966).
[6] J. I. G. Cadogan, *Quart. Rev.* **16**, 208 (1962).
[7] A. N. Strachan and F. E. Blacet, *J. Am. Chem. Soc.* **77**, 5254 (1955).
[8] H. E. Zimmerman and V. R. Sandel, *Ibid.* **85**, 915 (1963).
[9] E. S. Gould, *Mechanism and Structure in Organic Chemistry* p. 261. Holt, Reinhart and Winston, New York (1963).
[10] J. G. Calvert and J. N. Pittz, Jr., *Photochemistry* p. 825. Wiley, New York (1966).
[11] I. J. Borowitz, M. Anschel and S. Firstenberg, *J. Org. Chem.* **32**, 1723 (1967).
[12] H. Machleidt and G. U. Strehlke, *Angew. Chem.* **76**, 494 (1964).
[13] J. B. Plumb and C. E. Griffin, *J. Org. Chem.* **28**, 2908 (1963).

[14] A. H. Ford-Moore and B. J. Perry, *Org. Syntheses* Coll. Vol. IV; p. 955 (1963).
[15] F. G. Mann and D. Purdie, *J. Chem. Soc.* 1549 (1935).
[16] P. A. Levene and A. Walti, *J. Biol. Chem.* **79**, 363 (1928).
[17] W. Madelung and M. E. Oberwegner, *Chem. Ber.* **65**, 931 (1932).
[18] L. B. Cross and H. R. Henze, *J. Am. Chem. Soc.* **61**, 2730 (1939).
[19] N. E. Rigler and H. R. Henze, *Ibid.* **58**, 474 (1936).
[20] J. W. Farren, H. R. Fife, F. E. Clark and C. E. Garland, *Ibid.* **47**, 2419 (1925).
[21] R. P. Mariella and J. L. Leach, *Ibid.* **71**, 3558 (1949).
[22] W. Reeve and A. Sandle, *Ibid.* **72**, 1251 (1950).
[23] P. A. Leeve and A. Walti, *Org. Syntheses* Coll. Vol. II; p. 5 (1950).
[24] N. Kreuzkamp and H. Kayser, *Chem. Ber.* **89**, 1614 (1956).
[25] D. P. Evans, *J. Chem. Soc.* 1310 (1930).
[26] G. M. Kosolapoff, *Organophosphorus Compounds* p. 258. Wiley, New York (1950).
[27] B. C. Sander, G. J. Stacey, F. Wild and I. G. E. Wilding, *J. Chem. Soc.* 699 (1948).
[28] J. W. C. Peereboom, *J. Chromatog.* **2**, 323 (1960).