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Photochemical Studies of the Esters of Aroylphosphonic Acids

Ken-ichi TERAUCHI and Hiroshi SAKURAI

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka

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The photochemical behavior of several dialkyl benzoylphosphonates and *para*-substituted benzoylphosphonates in various solvents has been studied using product isolation, ultraviolet-spectral change, the electron spin resonance (ESR) technique, and quantum yield measurements. Upon irradiation to a degassed solution of these benzoylphosphonates through a Pyrex filter, the photo-pinacolization reaction was observed, except in the case of diethyl benzoylphosphonate; it was effectively quenched by 1,3-pentadiene or oxygen. On the other hand, the ESR spectra of photo-irradiated aroylphosphonates at 77°K have a large anisotropic doublet of 53—128 gauss separation; this separation is thought to be due to the interaction between an unpaired electron and the phosphorus nucleus. The structure of these radicals is also discussed. From these observations, it can be considered that the photochemical reaction proceeds *via* the ketyl radical formed by the hydrogen abstraction of the lowest excited triplet state of these aroylphosphonates. Irradiation to the diethyl benzoylphosphonate solutions in various solvents gave, not the pinacolized product, but 2,4,6-triphenyl-2,4,6-tris[diethylphosphoryl]-1,3,5-trioxane almost quantitatively. The quantum yields (Φ) of the disappearance of several *para*-substituted derivatives are highly sensitive to the electron-inductive abilities of the substituents; that is, Φ drops from 2.10 in the *p*-methoxybenzoylphosphonate derivative to 1.79 in the *p*-chloro derivative at room temperature. Such a substituent effect can be considered to result in the difference in the conformation between the carbonyl and phosphoryl groups. On the basis of these studies, the mechanism of the photochemical reaction of aroylphosphonates is described and discussed.

In a previous paper,[1] we demonstrated that dialkyl aroylphosphonates had a moderately strong n-π^* transition of the carbonyl group occurring around 320—390 mμ because of the interaction with the phosphorus d-orbitals. Therefore, as an extension of the previous work, we wish now to report on the photochemical behavior and on the reaction mechanism of these aroylphosphonates.

The photochemistry of organo-phosphorus derivatives has received only a little attention. In general, photochemical studies of organo-phosphorus compounds have been undertaken out of an interest in synthesis; that is, Griffin and his co-worker[2] have demonstrated the synthesis of a variety of nuclear

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[1] K. Terauchi and H. Sakurai, This Bulletin, **42**, 821 (1969).

[2] R. Obrycki and C. E. Griffin, *J. Org. Chem.*, **33**, 632 (1968).

substituted phenylphosphonates and other aryl-(1-naphthyl-, 2-thienyl-, 2-furyl-) phosphonates by the photolysis of the corresponding aryl iodides in an excess of trialkyl phosphite. Also, Petrellis and his co-worker[3] have reported that the irradiation of a solution of 1,3,2-dioxaphospholans in 2-methyl-2-butene or 2,3-dimethyl-2-butene provided the corresponding phenylcyanocyclopropanes. However, the study of the reactivity is important to the same extent for the photochemistry of organophosphorus compounds. From this point of view, we have studied the effect of substituents on the reactivity and the low-lying excited-state structure of these aroylphosphonates.

Results and Discussion

1) Irradiation to Dialkyl Benzoylphosphonates. Before describing the experimental results, it will be useful to clarify the primary photochemical process of dialkyl benzoylphosphonates.

The ultraviolet absorption spectra of a solution of dialkyl benzoylphosphonates are very similar to those of diethyl benzoylphosphonate.[1] The spectra of all the degassed cyclohexane solutions of dialkyl benzoylphosphonates were drastically altered by irradiation through a filter cutting off below 3200 Å; such a filter causes the light to be almost completely absorbed by only the n–π^* transition bands of benzoylphosphonates.

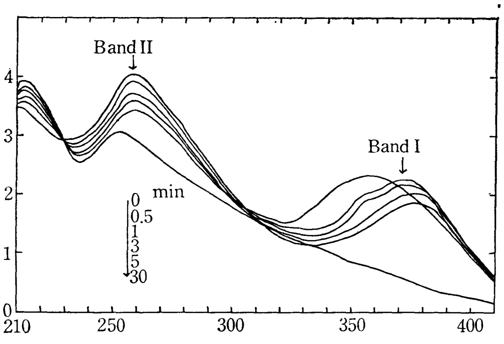


Fig. 1a. The progressive spectral change of diethyl benzoylphosphonate on irradiation in cyclohexane. Numbers refer to irradiation time.

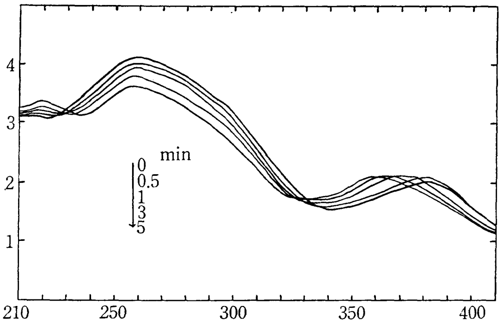
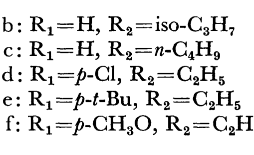


Fig. 1b. The progressive spectral change of di-n-butyl benzoylphosphonate on irradiation in cyclohexane. Numbers refer to irradiation time.

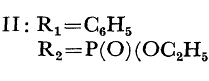
a) Photochemical Reactions of Diethyl Benzoylphosphonate. Figure 1a shows the progressive spectral change in a cyclohexane solution of diethyl benzoylphosphonate at an irradiation above 3200 Å. The absorption band II (258 mμ) decreased, and a new band appeared with maxima of 213 and 245 mμ, as the irradiation time increased. On the other hand, the I absorption band (379 mμ) increased with the hypsochromic shift and disappeared after 30 min, as is shown in Fig. 1a. One isosbestic point was observed, at 228 mμ. It may reasonably be considered that the increase in the n–π^* absorption is due to the formation of the ketyl radical or the kethyl radical ion, which might serve as reaction intermediates. Such an intensification of the n–π^* absorption has also been observed in a solution of the other aroylphosphonates used in the present work. The photoproduct, which had its absorption maxima at 213 and 245 mμ in a cyclohexane solution, as can be seen from Fig. 1a, was confirmed to 2,4,6-triphenyl-2,4,6-tris-[diethylphosphoryl]-1,3,5-trioxane (III) by a study of its infrared spectra, by elemental analysis, and by molecular-weight measurements.

b) Photochemical Reactions of Diisopropyl- and Di-n-butyl benzoylphosphonates. Figure 1b shows the progressive spectral change in a solution of di-n-butyl benzoylphosphonate. The absorption band II (259 mμ) decreased and a new band with the maximum of 220 mμ gradually appeared, but no clear isosbestic point was observed. As is shown in Fig. 1b, the absorption band I (380 mμ) increased for only the first 10 min in a pattern similar to that of diethyl benzoylphosphonate. A similar progressive spectral change was also observed in the case of diisopropyl benzoylphosphonate.

On the other hand, the photochemical reaction of diisopropyl- and di-n-butyl benzoylphosphonates solutions afforded the corresponding pinacols, IIb and IIc respectively, which were identified by means



$$\begin{array}{l} R_1\text{-}C_6H_4\text{-}\overset{\overset{H}{|}\ \overset{O}{|}}{C}\text{-}\overset{\overset{O}{\|}}{P}(OR_2)_2 \\ R_1\text{-}C_6H_4\text{-}\underset{\underset{H}{|}\ \underset{O}{|}}{C}\text{-}\underset{\underset{O}{\|}}{P}(OR_2)_2 \end{array}$$



IIb: R_1=H, R_2=iso-C_3H_7
c: R_1=H, R_2=n-C_4H_9
d: R_1=p-Cl, R_2=C_2H_5
e: R_1=p-t-Bu, R_2=C_2H_5
f: R_1=p-CH_3O, R_2=C_2H_5

III: R_1=C_6H_5
R_2=P(O)$(OC_2H_5)_2$

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[3] P. Petrellis and G. W. Griffin, *Chem. Commun.*, **1968**, 1099.

of elemental analysis, a study of their infrared and UV spectra, and molecular-weight measurements, as is shown in Tables 6 and 7.

2) Irradiation to *para*-Substituted Benzoylphosphonates. The photochemical reactions of three *para*-substituted benzoylphosphonates, *p*-chloro, *p*-*t*-butyl, and *p*-methoxy derivatives, were investigated in the same manner. The spectra of all the degassed cyclohexane solutions of *p*-substituted benzoylphosphonates were also markedly changed by irradiation.

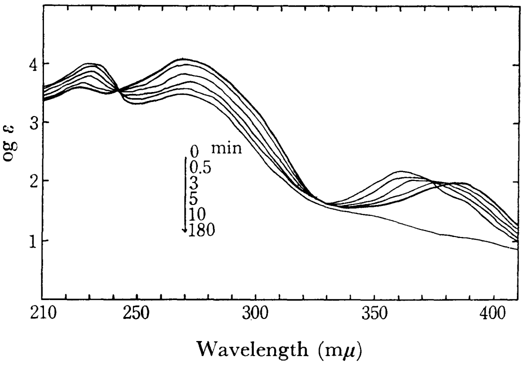


Fig. 2a. The progressive spectral change of diethyl *p*-chlorobenzoylphosphonate in cyclohexane. Numbers refer to irradiation time.

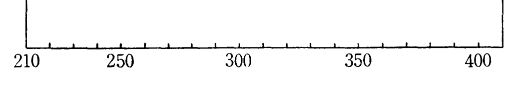


Fig. 2b. The progressive spectral change of diethyl *p*-methoxybenzoylphosphonate on irradiation in cyclohexane.
Numbers refer to irradiation time.

Photochemical Reactions of p-Chloro-, p-t-Butyl- and p-Methoxybenzoylphosphonates. The progressive spectral change in the absorption spectrum of *p*-chlorobenzoylphosphonate at an irradiation above 3200 Å is shown in Fig. 2a, where an isosbestic point is observed at 241 mμ. As the irradiation time increases, both the absorption bands, II (270 mμ) and I (385 mμ), decrease, and new bands, with maxima at 228 mμ and 360 mμ, appear. The new absorption band at 360 mμ, however, began to decrease at the irradiation time of 95 min and completely disappeared within 180 min.

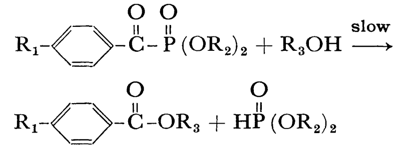
The isolated photoproduct from the irradiated solution was identified as the corresponding pinacol, IId. As is to be expected from the findings on the spectral change, this pinacol has only one high, intense band, at 228 mμ, with no shoulders in the 320—450 mμ region. Similar results have been observed from the experiments with *p*-*t*-butylbenzoylphosphonate.

On the other hand, in *p*-methoxybenzoylphosphonate the photoproduct had very poor solubility in cyclohexane at room temperature, and hence no data on the spectral change over 3 min could be obtained. Figure 2b shows the progressive spectral change in a solution of *p*-methoxybenzoylphosphonate. In this case, the II absorption band (295 mμ) decreased, new bands with maxima at 227 and 366 mμ appeared, and an isosbestic point was observed at 258 mμ.

3) Solvent Effects on the Photochemical Reactions. In order to examine the solvent effect on the photochemical reaction, irradiation through a Pyrex filter was carried out in degassed solutions of aroylphosphonates in various solvents at room temperature. The solvents used in this study were methanol, acetonitrile, carbon tetrachloride, benzene, *N*,*N*-dimethylformamide, dioxane, and *n*-pentane.

The results thus obtained are summarized in Table 8 in the Experimental section. As is obvious from Table 8, the photoproduct from the photolysis of the diethyl benzoylphosphonate solution was the trioxane derivative III in any solvent. On the other hand, the photolysis of di-*n*-butyl benzoylphosphonate under similar conditions in benzene, acetonitrile, and carbon tetrachloride afforded the pinacol IIc in every case much as in cyclohexane.

In the case of the methanol solution, we found, by the observation of the NMR and UV spectra, that the following reaction could proceed in the dark slowly at room temperature.



R_1=H, *p*-Cl, *p*-*t*-Bu, *p*-CH_3O
$R_2=C_2H_5$, iso-C_3H_7, *n*-C_4H_9
$R_3=CH_3$, C_2H_5, iso-C_3H_7

Further, it has been confirmed that any aroylphosphonate used in this study similarly reacts with alcohols, methanol, ethanol, and isopropyl alcohol. This reaction (for example, $R_1=H$, $R_2=C_2H_5$, $R_3=CH_3$) was observed to proceed to a 73% conversion in 17 hr in the dark at room temperature.

In addition, we could not find any evidence in these photochemical reactions for the corresponding products to undergo a Norrish type-I cleavage, that is, the predissociation of the C–P bond in the phosphonates by irradiation.

These results, obtained in various solvents, afford useful information on photochemical reaction mechanism. The finding of photopinacol formation in the aprotic solvents that the photochemical-excited state of di-*n*-butyl benzoylphosphonate must be able to abstract a hydrogen atom from the other phosphonate molecules to from ketyl radicals. Such a process are similarly suggested by the experiments on the quantum yield of aroylphosphonate disappearance in various solvents, as will be discussed in the next section. If this reaction is operative, the overall quantum yield of aroylphosphonate disappearance may then be greater than unity.

4) Quantum Yields of the Disappearance of Aroylphosphonates. *a) p-Substituted Aroylphosphonates.* The quantum yields of the disappearance of *p*-chloro-, *p*-*t*-butyl-, and *p*-methoxybenzoylphosphonates in a cyclohexane solution were determined in spectrophotometry. We found that the quantum yield of disappearance depended significantly upon the concentration of the solution in all cases; that is, the higher the concentration, the higher was the quantum yield obtained. A plot of the Φ^{-1} *vs.* the resiprocal of the phosphonate concentration is shown in Fig. 3.

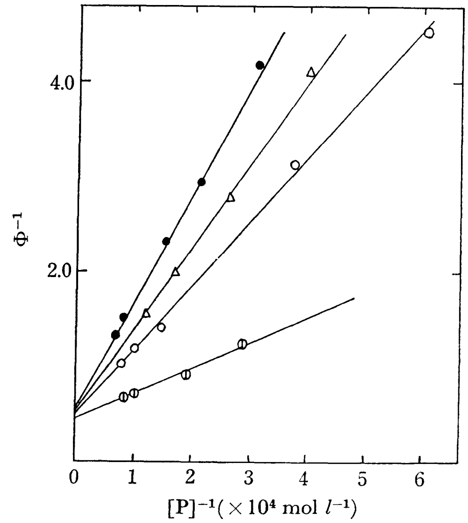


Fig. 3. Plot of Φ^{-1} against the reciprocal of diethyl *p*-substituted aroylphosphonate concentration.
● Cl; ○ $(CH_3)_3C$; △ H; ⦶ CH_3O

As can be seen from Fig. 3, the relation does result in a good linear relationship. These results are of particular interest. Although it is considered that many processes are probably operative in a photochemical reaction, a quantitative treatment of the dependence of quantum yield on the aroylphosphonate concentration will require knowledge concerning the extremely complex inhomogeneous distribution of radicals throughout the volume of the cell.

Furthermore, it was observed that the limited quantum yields of disappearance were significantly altered by the introduction of substituents into the aromatic ring of the phosphonate.

TABLE 1. SUBSTITUENT EFFECTS ON THE QUANTUM YIELD OF DISAPPEARANCE OF AROYLPHOSPHONATE

Substituent	Φ	σ
p-CH_3O	2.100	−0.268
p-$(CH_3)_3C$	2.000	−0.197
p-H	1.850	0
p-Cl	1.792	+0.227

The results obtained are shown in Table 1. Such a substituent effect on the quantum yield has previously been reported in *para*-substituted benzoylphosphonates by Pitts and his co-workers;[4] they demonstrated that the quantum yields of the disappearance of *para*-substituted benzophenones decreased with an increase in the electron-donating ability of the substituent.

However, as is shown in Table 1, we found that, on the contrary, the quantum yields of the disappearance of *para*-substituted aroylphosphonate dropped from 2.10 in *p*-methoxybenzoylphosphonate to 1.79 in *p*-chloro derivatives. This is also evident from Fig. 4, a plot of Φ *vs.* the Hammett σ constants, in which the trend toward a lower quantum yield with an increase in the σ value is pronounced.

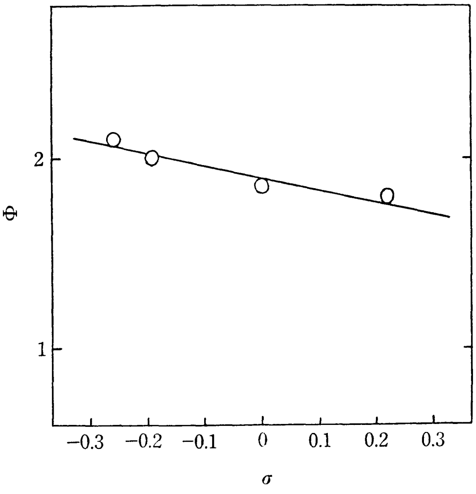


Fig. 4. Plot of Φ against Hammett σ values.

Assuming that a reduction of electronic density occurs on the carbonyl oxygen atom during an n–π^* transition, the Φ *vs.* σ relation indicates that

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[4] J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962); L. H. Piette, J. H. Sharp, T. Kuwana and J. N. Pitts, Jr., *J. Chem. Phys.*, **36**, 3094 (1962); E. J. Baum, J. K. S. Wan and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **88**, 2652 (1966).

electronwithdrawing substituents reduce the reactivity of the excited carbonyl group. These facts may be explained in terms of the steric effect concerning the preferred conformation in the aroylphosphonates. The NMR data suggest free rotation around the C–P bond.[5] Dipole-moment measurements have been reported the values of 2.93D for Ia, 3.20D for If, and 2.64D for Id.[6] These values of Id and If are lower and higher respectively than those of the corresponding aldehydes (reported[7] as 3.70D and 2.03D respectively), suggesting that the powerful electron-inductive abilities of the methoxy and chloro functions cause a change in the electron density on the carbonyl carbon atom. That is, the more the electron density on the carbonyl carbon increases, the more the life-time of the conformation in which the carbonyl and phosphoryl groups are opposite may increase. Therefore, it is reasonable to consider that the conformation between the carbonyl and phosphoryl groups can alter the intermolecular hydrogen atom-abstracting ability of the excited carbonyl group.

Although it is recognized that the quantum yield data indicate the excited state reactivities, while, on the other hand, the σ constants and the dipole moment involve ground states only, such a linear relationship between the Φ and σ values appears worthy of comment. Unfortunately, no kinetic data involving σ constants for *para*-substituted benzoylphosphonate in a reaction in which a hydrogen atom or ion is transferred have yet been reported.

However, such a substituent effect is significant and may apply to rate constants.

b) Quenching Effect of 1,3-Pentadiene and O_2. In order to examine this photoreduction mechanism, the effect of the addition of such a quencher as 1,3-pentadiene and oxygen, both of which are well-known as triplet quenchers, was investigated. The quenching efficiency of these additives was found to be significantly sensitive. The quantum yields of the di-*n*-butyl benzoylphosphonate disappearance against the 1,3-pentadiene (piperylene) concentrations are summarized in Table 2. The concentration of benzoylphosphonate was essentially constant throughout these measurements. As is obvious from Table 2, the quantum yield of disappearance in cyclohexane decreased markedly with an increase in the quencher concentration. A plot of Φ^{-1} *vs.* the quencher coccentrations is given in Fig. 5.

Table 2. Quenching effect of 1,3-pentadiene on photoreduction of 3.11×10^{-4}M cyclohexane solutions of di-*n*-butyl benzoylphosphonate

[1,3-Pentadiene] × 10^5	Φ
0	1.309
0.126	1.250
0.530	1.144
1.060	0.925
2.120	0.776

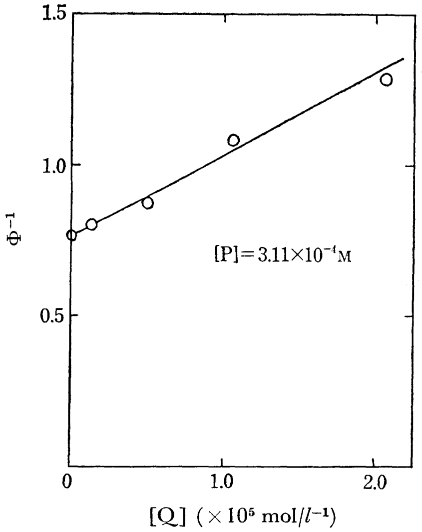

Fig. 5. Plot of Φ^{-1} against 1,3-pentadiene concentration.

A linear relationship of Φ^{-1} against the concentration of piperylene was obtained. Therefore, it is clear that the photochemical reaction proceeds *via* the excited triplet state of aroylphosphonate.

Moreover, the quenching effect of oxygen was examined. In a 1.14×10^{-4}M solution of di-*n*-butyl benzoylphosphonate, the value of the quantum yield of disappearance was 0.870 in a degassed solution, while in a nondegassed solution was 0.377; this observation may be considered to provide evidence for the quenching action of the presence of dissolved oxygen.

c) Solvent Effects on the Quantum Yield of Disappearance. The quantum yields of di-*n*-butyl benzoylphosphonate disappearance were determined in various solvents. The results obtained are summarized in Table 3. As can be seen from Table 3, the quantum yields of disappearance in aprotic solvents indicate smaller values than those in hydrogen-donating solvents. These facts suggest that the excited phosphonate molecule can be abstracting, to a smaller extent, a hydrogen atom from the solvent to form a ketyl radical. However, it should be noted that the quantum yield of disappearance indicates only a little variation depending on whether the solvent is hydrogen-deficient or -donating. As compared with the hydrogen-donating

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5) K. D. Berlin and H. A. Taylor, *J. Amer. Chem. Soc.*, **86**, 3862 (1964).

6) See Ref. 5. These values were measured in methyl esters.

7) L. G. Wesson, "Tables of Electric Dipole Moment," The Technology Press, Cambridge, Mass. (1948).

TABLE 3. THE QUANTUM YIELDS OF DISAPPEARANCE OF PHOSPHONATE IN VARIOUS SOLVENTS AT ROOM TEMPERATURE

Solvent	λ_{max} (mμ)	ε	Φ	conc. (mol·l^{-1})
Cyclohexane	259	12880	0.745	1.0×10^{-4}
Ether	259	8850	0.782	1.1×10^{-4}
n-Pentane	259	10380	0.752	1.0×10^{-4}
Acetonititle	261	7920	0.660	1.0×10^{-4}
Carbon tetrachloride	259	8990	0.621	1.0×10^{-4}

solvents, it would be reasonable to conclude that such a high quantum yield of disappearance in aprotic solvents implies the formation of ketyl radicals. As has been mentioned earlier, we know that the solvent effect in photochemical reaction is almost negligible. Consequently, it can be deduced that the excited triplet state of the phosphonate abstracts a hydrogen atom from other phosphonate molecules in the ground state in a photochemical reaction.

5) Electron Spin Resonance Spectra of Irradiated Aroylphosphonates. A low-temperature (77°K) ESR technique was used to investigate whether the triplet state of phosphonate could be detected. When a degassed solution of aroylphosphonate Ia-f was irradiated at 77°K with a filter transparent above 3200 Å, the ESR signal (at *ca.* 1500 gauss) attributable to the triplet state of benzoylphosphonate caused by the transitions between the highest and lowest sublevels and corresponding to $\Delta Ms=2$ was not detected. However, a strong phosphorescence was noted during irradiation in a rigid medium, and an ESR signal (at *ca.* 3000 gauss) attributable to a free radical species of benzoylphosphonate was observed at 77°K. These ESR spectra have a large anisotropic doublet of 53—128 gauss separation and a *g* value almost close to the free spin value.

In a previous paper,[8] we proposed, on the basis of the calculation of these signals, that the greater part of an unpaired electron was localized in the carbonyl carbon atom and was partially delocalized over the P–O group, perhaps through the vacant d orbitals on phosphorus.

In connection with the experimental results on the photochemical reactions in solution, it seems most reasonable to conclude that the structure of the observed radicals is previously postulated for the ketyl radical, which is produced by the hydrogen abstraction of an electron-deficient oxygen atom in the n–π^* triplet state of the carbonyl group in aroylphosphonate Ia-f.

6) Estimated Mechanism of Photopinacolization Reaction. On the basis of these studies, the possible photochemical reaction scheme of aroylphosphonates at an irradiation above 3200 Å can be written as is shown in Eqs. (1)—(8), where P, PH, Q, and RH are the phosphonate molecule, the ketyl radical, the quencher, and the solvent respectively.

$$\mathrm{P} \xrightarrow{h\nu} \mathrm{P}^* \tag{1}$$

$$\mathrm{P}^* + \mathrm{RH} \rightarrow \mathrm{PH} + \mathrm{R}\cdot \tag{2}$$

$$\mathrm{P}^* \rightarrow \mathrm{P} \tag{3}$$

$$\mathrm{P}^* + \mathrm{P} \rightarrow \mathrm{PH} + \mathrm{P}'\cdot \tag{4}$$

$$\mathrm{P}^* + \mathrm{Q} \rightarrow \mathrm{P} + \mathrm{Q}^* \tag{5}$$

$$\mathrm{P}'\cdot + \mathrm{RH} \rightarrow \mathrm{P} + \mathrm{R}\cdot \tag{6}$$

$$\mathrm{R}\cdot + \mathrm{P} \rightarrow \mathrm{PH} + \mathrm{R}' \tag{7}$$

$$2\mathrm{PH} \rightarrow \mathrm{P{-}P} \tag{8}$$

It is unlikely that the reaction (7) will occur in the solvents used in this study. The fact that the observed quantum yields of aroylphosphonate disappearance tend toward near 2 can be explained if the reaction (4) is operative. At high concentrations of phosphonate, reaction (4) is thought to become relatively more important.

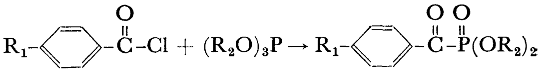
Finally, we are now investigating the reason why the difference in the alkyl function in the phosphoryl group or the introduction of *para*-substituents drastically changes the product in a photochemical reaction in solution.

Experimental

Preparation of Dialkyl Aroylphosphonates Ia-f. The acid chloride was stirred, drop by drop, into the trialkyl phosphite at 10—20°C in a nitrogen atmosphere. The temperature was raised slowly to room temperature during about a 1-hr period.

The reaction mixture was then distilled under reduced pressure to give dialkyl aroylphosphonate as a yellow oil. The data are listed in Table 4.

TABLE 4. PREPARATION OF AROYLPHOSPHONATES



Com- pound	R_1	R_2	bp		Yield %	Phosphite: Acid chloride
			°C	mm		
Ia	H	C_2H_5	142	1.0	70	4 : 3
Ib	H	iso-C_3H_7	127	0.8	55	4 : 3
Ic	H	*n*-C_4H_9	175	4.0	32	4 : 3
Id	*p*-Cl	C_2H_5	159	2.0	57	4 : 3
Ie	*p*-$(CH_3)_3C$	C_2H_5	163	0.8	29	4 : 3
If	*p*-CH_3O	C_2H_5	158	0.5	79	4 : 3

Repeated distillation under reduced pressure was used to purify all the compounds needed. The purity was confirmed by the presence of only one spot after development by the thin-layer chromatographic method. Carbon tetrachlorde, benzene, acetonitrile, *n*-hexane, *n*-pentane, dioxane, *N*,*N*-dimethylformamide (DMF),

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[8] K. Terauchi and H. Sakurai, This Bulletin, **42**, 2714 (1969).

methanol, and ethanol were purified by ordinary methods.

Steady-light Experiment. The light source employed was a Toshiba high-pressure mercury lamp (Model HLS-4002Å type), while for cutting off below 3200 Å a UV-35 Toshiba filter was used. Aliquots (4 ml) of solutions in various concentrations were pipetted into the Pyrex tube equipped with a quartz spectroscopic cell (path-length 10 mm) at the side-arm, and then tubes degassed in four cycles of the freeze-melt technique.

The absorption spectra were taken with a Hitachi EPU-2 spectrophotometer.

Measuremtnt of the Quantum Yield. The chemical change occurring in the photolyte was determined from the change in the optical density at the wavelength of the absorption maximum. The quantum yields of the disappearance of the photolyte were calculated from the form of the absorption spectrum before and after irradiation. The extinction coefficients of aroylphosphonates in cyclohexane which were used for the calculation of the quantum yields are given in Table 5.

TABLE 5. EXTINCTION COEFFICIENTS OF AROYLPHOSPHONATES IN CYCLOHEXANE

Compound	$\lambda_{\max}$ (mμ)	ε, l mol^{-1}·cm^{-1}
Ia	258	11220
	379	83
Ib	258	11880
	379	82
Ic	259	12880
	380	103
Id	268	12600
	385	93
Ie	271	11500
	375	145
If	294	10250
	373	152

The amount of irradiation absorbed by the solution was determined by the use of a potassium ferrioxalate actinometer[9] with filtered irradiation from a Toshiba high-pressure mercury lamp (HLS-4002A). After irradiation, aliquots of the ferrioxalate solution were treated with phenanthroline and analyzed for the ferrous ion. The mean value for the irradiation absorbed was 3.22×10^{16} quanta/sec without the photolyte solution and 3.189×10^{16} quanta/sec with the photolyte solution. The difference between these two quantities, 3.507×10^{14} quanta/sec, is the quantity of irradiation absorbed by the aroylphosphonate solution.

General Procedure of the Photolysis of Aroylphosphonates in Cyclohexane. A mixture of 1.0 g of aroylphosphonate and 30 ml of cyclohexane in a Pyrex tube was degassed by the freezement technique and then irradiated with a 400-Watt high-pressure mercury are at room temperature. The irradiation was carried out until the yellow color of the solution was entirely bleached out. After irradiation evaporating the solvent at reduced pressure, either a white solid or a colorless, oily photoproduct was obtained. These products were dried under a high vacuum for several hours. The analytical and spectral data of these photoproducts are summarized in Tables 6 and 7.

TABLE 6. ANALYTICAL DATA FOR THE PHOTOPRODUCTS FROM AROYLPHOSPHONATES Ib—f

Compound	Irrad. hr	Formula	Molecular weight* Found	Calcd.	Anal. Found (Calcd) C (%)	H (%)	P (%)
Ib	5	$C_{26}H_{40}O_8P_2$	551	542	57.22	7.37	11.42
					(57.50	7.37	11.44)
Ic	5	$C_{30}H_{48}O_8P_2$	596	598	59.98	8.25	9.96
					(60.20	8.02	10.37)
Id	4	$C_{22}H_{30}O_8P_2Cl_2$	553	555	47.29	5.88	11.50
					(47.56	5.40	11.79)
Ie	5	$C_{30}H_{48}O_8P_2$	589	598	59.88	8.27	10.30
					(60.20	8.02	10.37)
If	4	$C_{24}H_{36}O_{10}P_2$	544	546	52.52	6.60	11.47
					(52.74	6.59	11.35)

* Measured by the vapor phase osmometry in benzene at 45°C.

TABLE 7. THE SPECTRAL DATA FOR THE PHOTOPRODUCTS FROM AROYLPHOSPHONATES Ib—f

Compound	IR (cm^{-1})	UV ($\lambda_{\max}$ mμ, log ε)
Ib	3300 (ν OH), 1595 (phenyl), 1380 (δ_s CH_3), 225 (ν P=O), 1130, 1020 (P-O-C)	240 (3.11) alone
Ic	3200 (ν OH), 1595 (phenyl), 1225 (ν P=O), 1130, 1025 (P-O-C)	237 (3.01) alone
Id	3300 (ν OH), 1588 (phenyl), 1220 (ν P=O), 1160, 1010 (P-O-C)	224*(4.11), 268*(3.79)
Ie	3300 (ν OH), 1595 (phenyl), 1225 (ν P=O), 1160, 1015 (P-O-C)	228 (4.19), 266 (3.40)
If	3350 (ν OH), 1590 (phenyl), 1230 (ν P=O), 1160, 1020 (P-O-C)	288*(3.52)alone

* Measured in acetonitrile solution.

On the basis of these data, the photoproducing agent was identified as the pinacol II. The treatment of the photopinacol II with dilute or concentrated hydrochloric acid in an attempt to produce the phosphonic acid derivative was unsuccessful, giving only tar. After alkaline hydrolysis with a 17% potassium hydroxide solution, treatment with 2,4-dinitrophenylhydrazine in ethanol gave the hydrazone derivatives. This hydrazone was washed by 20% aqueous methanol and dried under reduced pressure over calcium chloride. The benzaldehyde 2,4-dinitrophenylhydradrazone

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[9] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, **A235**, 518 (1956).

melted at 241—242°C (lit, mp 237°C). These observation suggest that the pinacol undergoes carbon-carbon bond cleavage to form the α-hydroxy phosphonic ester, which is then further hydrolyzed by the excess base to yield the aldehyde.

Photolysis of Ia and Ic in Various Solvents. The photolyses were carried out by a similar method. The analytical data of the photoproducts are summarized in Table 8.

The IR spectrum of the photoproduct from no solution of Ia showed any carbonyl absorption. IR(KBr disk); 1600, 1440 (phenyl), 1220 (P=O), 1160, and 1020 (P–O–C) cm^{-1}. The UV spectrum had only one high intense band ($\lambda_{max}^{CH_3CN}$ 245 mμ, log ε 3.27), with no shoulders in the 280—450 mμ region. Attempts to lead from this compound to the phosphonic acid by acid or alkaline hydrolysis under any conditions were unsuccessful.

No useful information on the structure could be obtained from the NMR spectrum. Although the structure of the trimer contains several configurations, the structure, III, we have proposed seems to accord best with the observed data.

On the other hand, the product from Ic was identified as the IIc pinacol by means of the same spectral data, as is shown in Table 7, and by means of the analytical data (Table 8).

Table 8. Analytical data for the photoproducts from Ia and Ic in various solvents

Compound irradiated	Solvent	Irrad. hr	Molecular weight* Found	Anal. Found C (%)	H (%)	P (%)
Ia	Cyclohexane	5	721	54.28	6.41	12.72[a]
	n-Pentane	5	724	54.38	6.29	12.60
	Acetonitrile	6	725	54.10	6.19	12.58
	Dioxane	5	722	54.29	6.37	12.55
	CCl_4	10	724	54.22	6.43	12.59
	Benzene	5	725	54.28	6.28	12.66
	DMF	8	718	54.24	6.55	12.49
Ic	Acetonitrile	5	597	59.55	8.32	10.11[b]
	Benzene	5	591	59.80	8.22	10.26
	CCl_4	10	592	59.92	8.27	10.17

a) Calcd for $C_{33}H_{45}O_{12}P_3$: Mol wt; 726, C, 54.54; H, 6.20; P, 12.81%.

b) Calcd for $C_{30}H_{48}O_8P_2$: Mol wt; 598, C, 60.20; H, 8.02; P, 10.37%.

* Measured by the vapor phase osmometry in benzene at 45°C.