BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1473—1477 (1970)

The Photoreaction of *p*-Substituted *β*-Benzoylacrylic Acids

Noboru Sugiyama, Choji Kashima, Hiroshi Kataoka and Keiko Tanaka

Department of Chemistry, Tokyo Kyoiku University, Otsuka, Bunkyo-ku, Tokyo

(Received October 3, 1969)

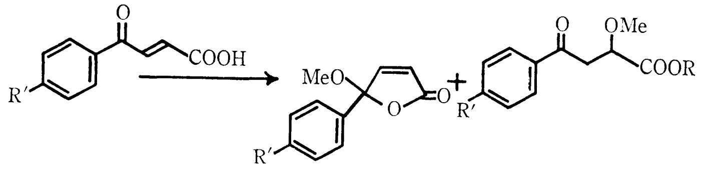
This paper will describe the photoreaction of *trans-β-(p*-ethylbenzoyl)acrylic acid (II) in methanol to give 5-(*p*-ethylphenyl)-5-methoxy-2-oxo-2,5-dihydrofuran (III), *β*-(*p*-ethylbenzoyl)-*α*-methoxypropionic acid (IV), and its methyl ester (V). The kinetic study of this reaction has revealed that II gives III and IV parallel by the first-order reaction and that IV then changes into V. Furthermore, the irradiation of *p*-substituted *β*-benzoylacrylic acids has been studied. From the product ratio and the substituent effects at the *para* position, the mechanism of the photoreactions of *γ*-oxoacrylic acids in methanol is proposed. This mechanism is also supported by the HMO calculations.

In our previous report[1] on the photoreaction of *β*-benzoylacrylic acid (I), a *γ*-oxoacrylic acid, in methanol, the formation of the methanol-addition product, *β*-benzoyl-*α*-methoxypropionic acid, and the reaction mechanism were described. However this mechanism is not sufficient to explain the photoreaction of *β*-acylacrylic acid, another *γ*-oxoacrylic acid, because *β*-acrylacylic acid is isomerized to 5-alkyl-5-hydroxy-2-oxo-2,5-dihydrofuran by irradiation.[2] Thus, we have examined the photoreaction of *p*-substituted *β*-benzoylacrylic acids in order to find a mechanism appropriate for all *γ*-oxo-acrylic acids.

Results and Discussion

Photoreaction of *β*-(*p*-Ethylbenzoyl)-acrylic Acid in Methanol. As a typical *p*-substituted *β*-benzoylacrylic acid, *β*-(*p*-ethylbenzoyl)acrylic acid (II) was chosen for the kinetic study. The structure of II was confirmed to be of the *trans* form by the coupling constant[1,2] of the olefinic protons (16.4 Hz) in the NMR spectrum. A methanol solution of II was irradiated with a 500-W high pressure mercury lamp for 105 hr at room temperature. From the reaction mixture after 80 hr irradiation, 5-methoxy-2-oxo-2,5-dihydrofuran (III), *β*-(*p*-ethylbenzoyl)-*α*-methoxy-propionic acid (IV) and the methyl ester (V) were obtained (Fig. 1). The yields of III, IV, and V were 27, 4, and 63% respectively.

The structures of these new photoproducts were determined as follows. The IR spectrum of III shows angelica lactone bands at 1820, 1780, and 1680 cm^{-1}, and the UV spectrum shows the absorption maximum at 243 nm. In the NMR spectrum the triplet signal at τ 8.77 was coupled with the quartet signal at τ 7.34 and the singlet signal



R′			R=H	R=Me
H	I			
Et	II	III	IV	V
Me	VII	XXI		XIV
i-Pr	VIII			XV
t-Bu	IX			XVI
MeO	X			XVII
EtO	XI			XVIII
Br	XII			XIX
Cl	XIII			XX

Fig. 1

---

[1] N. Sugiyama, H. Kataoka, C. Kashima and K. Yamada, This Bulletin, **42**, 1353 (1969).

[2] N. Sugiyama, H. Kataoka, C. Kashima and K. Yamada, *ibid.*, **42**, 1098 (1969).

corresponding to 3 protons appeared at τ 6.58. The signal at τ 3.91 was split to a doublet with a coupling constant of 6.0 Hz, and the multiplet of 5 protons appeared in the τ 2.36—3.16 region. From these spectral data and elemental analyses, the structure of III was deduced. The structure of V was determined by the IR, UV, and NMR spectra and by elemental analyses. These spectral data were then checked with the corresponding data of methyl β-benzoyl-α-methoxypropionate.$^{1)}$ IV was methylated with diazomethane, and the product was identified with V.

For the sake of comparison, the reaction without any irradiation and the thermal reaction of II in methanol were carried out. When a methanol solution of II was placed in a dark place for 24 hr, it was found to be 12% methyl *trans*-β-(*p*-ethylbenzoyl)-acrylate (VI) and 88% II. When refluxed for 24 hr in methanol, II was converted into 36% V and 64% VI. Thus, it was recognized that the formation of III, IV, and V from II was induced by the irradiation. The formation of an angelica-lactone-type compound, III, by the irradiation of II suggested that this photoreaction is different from that of I or β-acylacrylic acid.$^{1,2)}$

In order to get some information on the reaction mechanism, the behavior of methyl *trans*-β-(*p*-ethylbenzoyl)acrylate (VI) was studied. By irradiation, VI was transformed into a *cis* isomer in a 87% yield, but when refluxed in methanol VI did not show any change. When the photoreaction of II in methanol was examined by means of the NMR spectra, it was observed that II was gradually converted into III and IV. The results are summarized in Fig. 2. The yield of IV reached its maximum after 20 hr, and then decreased. However the total yield of the alcohol adducts, IV and V, increased when the first-order reaction with $k_1=8.9\times10^{-6}\,\text{sec}^{-1}$. The decrease curve of II showed a first-order reaction of II with $k=k_1+k_3=13.3\times10^{-6}\,\text{sec}^{-1}$, and the curve of III showed $k_3=4.4\times10^{-6}\,\text{sec}^{-1}$. Moreover, III in methanol did not change upon irradiation or refluxing. From these results, it can be assumed that the irradiation of II produces two parallel photoproducts, III and IV, and that IV changes into V.

On the other hand, it has been shown that the photoreaction of I does not occur in acidic or basic methanol, and that *cis*-β-benzoylacrylic acid (I′) is the intermediate of this reaction.$^{1)}$ Also, it is well known that maleic acid has a partial grouping similar to that of I′ and that it has an intramolecular hydrogen bonding with a seven-membered cyclic ring between the γ-carbonyl and carboxyl groups.$^{3)}$ From these facts, it can be assumed that the first step of the alcohol addition of *cis*-β-benzoylacrylic acids is the protonation on γ-carbonyl oxygen, and that γ-carbon becomes a carbonium ion, which makes it possible to represent by a resonance hybrid with a carbonium ion at the γ- or α-position. When a methanol molecule attacks the α-carbonium ion, the alcohol adducts will be formed, and when a methanol molecule attacks the γ-carbonium ion, the hemiketal of β-benzoylacrylic acids will be formed. These hemiketals can be cyclized to an angelica-lactone-type compound with ease. Consequently, the preponderance of the carbonium ion at the γ-position will result in the formation of an angelica-lactone-type compound, while that of the carbonium ion at the α-position will result in the formation of alcohol adducts.

Photoreaction of Other *p*-Substituted β-Benzoylacrylic Acids in Methanol. Since it is probable that the substituents at the *para* position of *p*-substituted β-benzoylacrylic acids will affect the preponderance of the carbonium ion at the γ- or α-position, the photoreactions of *p*-substituted derivatives of *trans*-β-benzoylacrylic acid were carried out in methanol. The derivatives used were *trans*-β-benzoylacrylic acid (I), *trans*-β-(*p*-toluoyl)acrylic acid (VII), *trans*-β-(*p*-isopropylbenzoyl)acrylic acid (VIII), *trans*-β-(*p*-*t*-butylbenzoyl)acrylic acid (IX),

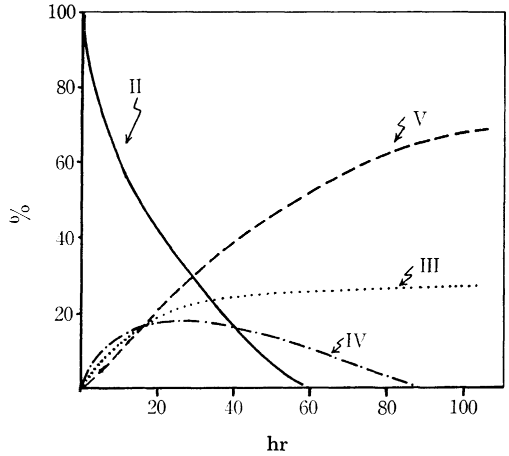


Fig. 2

TABLE 1. THE NMR SPECTRAL SIGNALS OF OLEFINIC PROTONS OF *p*-SUBSTITUTED β-BENZOYLACRYLIC ACID

Compd.	R′	$\tau_{\mathrm{H}\alpha}$	$\tau_{\mathrm{H}\beta}$	$J_{\mathrm{H}\alpha\mathrm{H}\beta}$
I	H	3.16	2.05	13.7 Hz
VII	Me	3.17	2.04	15.0
II	Et	3.20	2.04	16.4
VIII	*i*-Pr	3.19	2.06	15.2
IX	*t*-Bu	3.18	2.04	15.7
X	MeO	3.18	2.01	13.7
XI	EtO	3.18	2.03	16.1
XII	Br	3.26	2.14	13.7
XIII	Cl	3.18	2.06	15.7

---

3) F. H. Westheimer and O. T. Benfey, *J. Amer. Chem. Soc.*, **78**, 5309 (1956).

trans-β-(*p*-anisoyl)acrylic acid (X), *trans-β*-(*p*-ethoxybenzoyl)acrylic acid (XI), *trans-β*-(*p*-bromobenzoyl)-acrylic acid (XII), and *trans-β*-(*p*-chlorobenzoyl)-acrylic acid (XIII), all of them prepared by the method of Papa.[4] Their NMR spectra are shown in Table 1. The coupling constants[1,2] of the olefinic protons in the NMR spectra confirm that the structures of these *β*-benzoylacrylic acids have *trans* configurations.

The methanol solutions of these acids were irradiated with a 500-W high-pressure mercury lamp at room temperature. The reaction mixtures were separated by column chromatography, and the structures of these photoproducts were determined by a study of the IR, UV, and NMR spectra and by elemental analyses. The structure of each *p*-substituted *β*-benzoyl-*α*-methoxypropionic acid was determined to be that of the methyl ester obtained by treatment with diazomethane. Moreover, the yields of these photoproducts were determined by measuring the NMR spectra of the reaction mixtures (Fig. 1 and Table 2).

Table 2. The yield of the photoproducts from *p*-substituted *trans-β*-benzoylacrylic acid in methanol

Starting compd.	Material R′	Time (hr)	Photoproducts		
			Angelica lactone	Alcohol adducts	
				Acid	Ester
			(%)	(%)	(%)
I	H	120	0	100	0
VII	Me	120	23	0	77
II	Et	168	17	4	76
VIII	*i*-Pr	168	10	70	15
IX	*t*-Bu	168	0	92	8
X	MeO	182	0	64	0
XI	EtO	168	0	89	11
XII	Br	168	trace	0	91
XIII	Cl	168	9	16	58

The methanol-addition reaction was observed in all cases. In the cases of the *p*-alkyl (except *t*-Bu) and *p*-halogeno *β*-benzoylacrylic acids, however 4-methoxy angelica-lactone-type compounds were produced.

From the results of the photo-reaction of *p*-alkyl *β*-benzoylacrylic acids, the hyperconjugation of alkyl groups at the *para* position appeared to have an effect on the yield of the angelica-lactone-type compounds. As is shown in Table 2, the stronger the hyperconjugation effect (Me>Et>*iso*-Pr>*t*-Bu), the higher was the yield of the angelica-lactone-type compound (VII>II>VIII>IX) observed.

Table 3. The Sr^N values of *p*-substituted *β*-benzoylacrylic acids

Compd.	R′	$Sr^N(\alpha)$	$Sr^N(\gamma)$	$Sr^N(\gamma)/Sr^N(\alpha)$
VII	Me	6.3326	5.9856	0.9452
XII	Br	6.2731	5.9264	0.9449
XIII	Cl	6.2514	5.9044	0.9445
X	MeO	5.2183	4.8764	0.9345

The carbonium ion at the *γ*-position can be expected to be preponderant because of the hyperconjugation of the *para* substituents. Thus, the above assumption of the favored formation of angelica-lactone compounds by the preponderance of the carbonium ion at the *γ*-position seems to be reasonable.

Furthermore, in order to support this assumption, the Sr values for the nucleophilic reagent (Sr^N) of zwitter-ion-type intermediates from VII, X, XII, and XIII were calculated by means of the HMO method. These Sr^N values indicate the stability of the carbonium ion and its reactivity toward nucleophilic reagents. Thus, the ratios of the Sr^N for the *α*-position to that for the *γ*-position, $Sr^N(\alpha)/Sr^N(\gamma)$, which are listed in Table 3, are expected to be comparable with the production ratio between the angelica-lactone-type compound and the alcohol adduct. The $Sr^N(\alpha)/Sr^N(\gamma)$ ratio of VII is large, and that of X is small, while the yield of the angelica-lactone-type compound from VII was high and no angelica-lactone-type compound from X was detected. These results also supported the above assumption.

After all, the photoreaction mechanism of the *γ*-oxoacrylic acid system is concluded to be as is shown in Fig. 3. That is, *trans* acid is isomerized

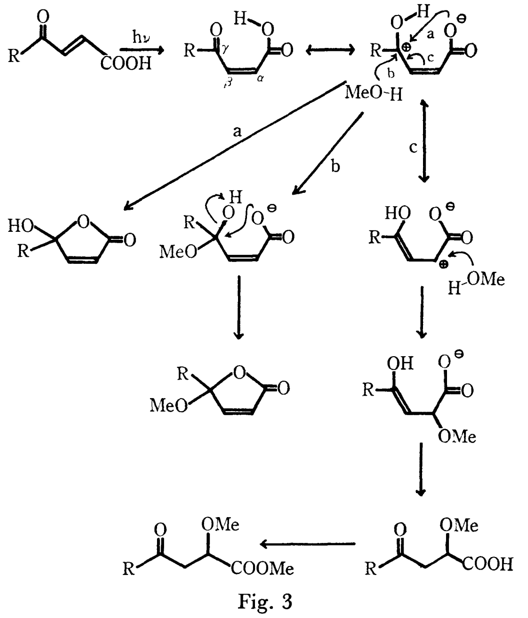


Fig. 3

---

[4] D. Papa, E. Schwenk, F. Villani and E. Klingsberg, *ibid.*, **70**, 3356 (1948).

to *cis* acid, which then undergoes protonation on γ-carbonyl oxygen through the seven-membered cyclic ring by means of intramolecular hydrogen bonding. By the protonation, the carboxyl group becomes the carboxylate anion and γ-carbon becomes the carbonium cation. In the case of β-aroylacrylic acids, this carbonium ion at the γ-position is dominated by the phenyl group and is attacked by the methanol molecule to give a hemiketal, which is then lactonized to 5-aryl-5-methoxy-2-oxo-2,5-dihydrofuran. At the same time, the carbon atom at the α-position can behave as a carbonium ion by means of resonance. The carbonium ion at the α-position is, then, attacked by a methanol molecule to give alcohol adducts. In the last step, the acid of the alcohol adduct is esterified.

In the case of β-acylacrylic acid, the carbonium ion at the γ-position is not stabilized and is attacked by the carboxylate anion. Thus, the production of 5-alkyl-5-hydroxy-2-oxo-2,5-dihydrofuran is also reasonable.

Experimental

Materials. p-Substituted *trans*-β-benzoylacrylic acids were prepared by the method of Papa.[4]

trans-β-Benzoylacrylic Acid (I). Mp 94—95.5°C (lit, 98—99°C). $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 237 (10370), 268 (8080) and 357 nm (86). $\tau^{\mathrm{CDCl_3}}$: 1.31 (s, 1H), 2.05 (d, 1H), 1.8—2.7 (m, 5H) and 3.16 (d, 1H).

trans-β-(p-Ethylbenzoyl)acrylic Acid (II). Mp 104—106°C (lit, 105—106°C). $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 233 (12460), 287 (10800) and 364 nm (125). $\tau^{\mathrm{CDCl_3}}$: 2.07 (d, 1H), 2.13 (d, 2H), 3.20 (d, 1H), 7.28 (q, 3H) and 8.67 (t, 2H).

trans-β-(p-Toluoyl)acrylic Acid (VII). Mp 137—139°C (lit, 137.5—138.5°C). $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 237 (12300), 286.5 (11700) and 370 nm (104). $\tau^{\mathrm{CDCl_3}}$: 0.31 (s, 1H), 2.04 (d, 1H), 2.08 (d, 2H), 2.70 (d, 2H), 3.17 (d, 1H) and 7.53 (s, 3H).

trans-β-(p-Isopropylbenzoyl)acrylic Acid (VIII). Mp 100.5—102°C. $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 234 (12700), 285.5 (11700) and 360 nm (127). $\tau^{\mathrm{CDCl_3}}$: 2.06 (d, 1H), 2.12 (d, 2H), 2.72 (d, 2H), 3.19 (d, 1H), 9.04 (sept, 1H) and 8.73 (d, 6H).

trans-β-(p-t-Butylbenzoyl)acrylic Acid (IX). Mp 122—124°C (lit, 123—125°C). $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 234 (13200), 287 (12500) and 364 nm (124). $\tau^{\mathrm{CDCl_3}}$: 2.04 (d, 1H), 2.09 (d, 2H), 2.54 (d, 2H), 3.18 (d, 1H) and 8.64 (s, 9H).

trans-β-(p-Anisoyl)acrylic Acid (X). Mp 134°C (lit, 138—139°C). $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 233 (17400) and 314 (13900). $\tau^{\mathrm{CDCl_3}}$: 1.60 (s, 1H), 2.01 (d, 1H), 2.01 (d, phenyl 2H), 3.07 (d, 1H), 3.18 (d, 1H) and 6.13 (s, 3H).

trans-β-(p-Ethoxybenzoyl)acrylic Acid (XI). Mp 142.5—145°C (lit, 145.5—146.5°C). $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 235.5 (16800) and 315 nm (13200). $\tau^{\mathrm{CDCl_3}}$: 2.03 (d, 1H), 2.04 (d, 2H), 3.07 (d, 2H), 3.18 (d, 1H), 5.87 (q, 2H) and 8.55 (t, 3H).

trans-β-(p-Bromobenzoyl)acrylic Acid (XII). Mp 154—156°C (lit, 154—155°C). $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 249 (10070), 278 (8390) and 362 nm (73). $\tau^{\mathrm{CDCl_3}}$: 2.06 (d, 2H), 2.17 (d, 1H), 2.54 (d, 2H) and 3.18 (d, 1H).

trans-β-(p-Chlorobenzoyl)acrylic Acid (XIII). Mp 157—159°C (lit. 159—160°C). $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 230 (14500) and 282 nm (13000). $\tau^{\mathrm{CDCl_3}}$: 2.13 (d, 2H), 2.14 (d, 1H), 2.37 (d, 2H) and 3.26 (d, 1H).

Instrumentation. The infrared and ultraviolet spectra were recorded on a Hitachi EPI-2-type infrared spectrometer and a Hitachi EPS-3T-type spectrometer respectively. The NMR spectra were recorded on a Hitachi H-60 high-resolution NMR spectrometer, using TMS as the internal standard. A Taika 500-W hgih pressure mercury lamp was used as the irradiation source, and a Pyrex tube was used as the filter and reaction vessel in the reactions.

The Calculation of the Sr values by Means of the HMO Method. The Sr values in this work were calculated by means of the HMO method on a Hypac 103-type computer, using the following parameter:[5]

$$\alpha_{\mathrm{X}} = \alpha + a\beta$$

$$\alpha_{\mathrm{adj}} = \alpha + b\beta$$

$$\beta_{\mathrm{cx}} = l\beta$$

X	*a*	*b*	*l*
OH	0.6	0	0.7
Me	3	−0.1	1
OMe	0.5	0	0.6
Br	1.4	0	0.7
Cl	1.8	0	0.8
C=O	1.3	0	1.1

Irradiation of p-Substituted *trans*-β-Benzoylacrylic Acid in Methanol. A solution of 1 g of p-substituted *trans*-β-benzoylacrylic acid in 20 m*l* of methanol in a Pyrex tube was irradiated at room temperature. After the reaction mixture had been worked up by the usual method, the yields of the products were estimated by the intensity of the NMR signals at τ 3.2 (d, olefinic proton of acrylic acid), 3.9 (d, α-olefinic proton of angelica lactone), 5.6 (t, methine proton of alcohol adducts), and 6.3 (s, ester methyl protons of the ester of the alcohol adducts). At the same time, the residue was methylated with diazomethane in ether. Then the reaction products were chromatographed on a silica-gel column with a benzene-ethyl acetate mixture.

Methyl β-(p-Ethylbenzoyl)-α-methoxypropionate (V). ν^{film}: 1745, 1675 and 1605 cm^{-1}. $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 254.5 (17500) and 315.5 nm (117). $\tau^{\mathrm{CDCl_3}}$: 2.14 (d, 2H), 2.76 (d, 2H), 5.57 (t, 1H), 6.26 (s, 3H), 6.56 (s, 3H), 6.63 (d, 2H), 7.23 (q, 2H) and 8.78 (t, 3H).

Found: C, 67.18; H, 7.25%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%.

Methyl β-(p-Toluoyl)-α-methoxypropionate (XIV). ν^{film}: 1740, 1675, 1600 and 805 cm^{-1}. $\lambda_{\max}^{\mathrm{EtOH}}$ (ε): 254 (19400), 290 (830) and 319 nm (107). $\tau^{\mathrm{CDCl_3}}$: 2.08 (d, 2H), 2.72 (d, 2H), 5.52 (t, 1H), 6.18 (s, 3H), 6.48 (s, 3H), 6.59 (d, 2H) and 7.56 (s, 3H).

Found: C, 65.86; H, 6.86%. Calcd for $C_{13}H_{16}O_4$:

---

[5] a) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951). b) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952). c) A. Streiweisser, Jr., and P. M. Nair, "Conference of Hyperconjugation," Pergamon Press, London (1959).

C, 66.08; H, 6.83%.

Methyl β-(p-Isopropylbenzoyl)-α-methoxypropionate (XV). ν^{film}: 1755, 1685 and 1610 cm^{-1}. $\lambda_{\text{max}}^{\text{EtOH}}$ (ε): 255 (20900) and 316 nm (123). τ^{CDCl_3}: 2.14 (d, 2H), 2.74 (d, 2H), 5.57 (t, 1H), 6.23 (s, 3H), 6.54 (s, 3H), 6.66 (d, 2H), 7.06 (sept, 1H) and 8.74 (d, 6H).

Found: C, 68.08; H, 7.67%. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63%.

Methyl β-(p-t-Butylbenzoyl)-α-methoxypropionate (XVI). ν^{film}: 1755, 1685 and 1610 cm^{-1}. $\lambda_{\text{max}}^{\text{EtOH}}$ (ε): 254.5 (20000) and 315.5 nm (118). τ^{CDCl_3}: 2.13 (d, 2H), 2.57 (d, 2H), 5.57 (t, 1H), 6.24 (s, 3H), 6.56 (s, 3H), 6.66 (d, 2H) and 8.67 (s, 9H).

Found: C. 69.19; H. 8.07%. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97%.

Methyl β-(p-Anisoyl)-α-methoxypropionate (XVII). ν^{film}: 1760, 1685 and 1610 cm^{-1}. $\lambda_{\text{max}}^{\text{EtOH}}$ (ε): 219 (6095) and 274 nm (9225). τ^{CDCl_3}: 2.03 (d, 2H), 3.09 (d, 2H), 5.57 (t, 1H), 6.16 (s, 3H), 6.22 (s, 3H), 6.68 (d, 2H) and 6.54 (s, 3H).

Found: C, 61.67; H, 6.58%. Calcd for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39%.

Methyl β-(p-Ethoxybenzoyl)-α-methoxypropionate (XVIII). ν^{film}: 1750, 1675 and 1600 cm^{-1}. $\lambda_{\text{max}}^{\text{EtOH}}$ (ε): 219 (11900) and 276 nm (18700). τ^{CDCl_3}: 2.14 (d, 2H), 3.14 (d, 2H), 5.58 (t, 1H), 5.94 (q, 2H), 6.25 (s, 3H), 6.59 (s, 3H), 6.67 (d, 2H) and 8.59 (t, 3H).

Found: C, 63.07; H, 6.96%. Calcd for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81%.

Methyl β-(p-Bromobenzoyl)-α-methoxypropionate (XIX). ν^{film}: 1750, 1685, 1585 and 815 cm^{-1}. $\lambda_{\text{max}}^{\text{EtOH}}$ (ε): 257 (20100) and 289.5 nm (944). τ^{CDCl_3}: 2.13 (d, 2H), 2.41 (d, 2H), 5.55 (t, 1H), 6.22 (s, 3H), 6.52 (s, 3H) and 6.63 (d, 2H).

Found: C, 48.01; H, 4.36%. Calcd for $C_{12}H_{13}O_4Br$: C, 47.85; H, 4.36%.

Methyl β-(p-Chlorobenzoyl)-α-methoxypropionate (XX). ν^{film}: 1745, 1685 and 1590 cm^{-1}. $\lambda_{\text{max}}^{\text{EtOH}}$ (ε): 253.5 (19000) and 313 nm (89). τ^{CDCl_3}: 2.16 (d, 2H), 2.63 (d, 2H), 5.59 (t, 1H), 6.24 (s, 3H), 6.56 (s, 3H) and 6.66 (d, 2H).

Found: C, 56.09; H, 5.24%. Cacld for $C_{12}H_{13}O_4Cl$: C, 56.14; H, 5.11%.

5-*(p-Ethylphenyl)*-5-*methoxy*-2-*oxo*-2,5-*dihydrofuran (III).* ν^{film}: 1820, 1780, 1680 and 1605 cm^{-1}. $\lambda_{\text{max}}^{\text{EtOH}}$ (ε): 243 nm (5000). τ^{CDCl_3}: 2.36—3.16 (m, 5H), 3.91 (d, 1H), 6.58 (s, 3H), 7.34 (q, 2H) and 8.77 (t, 3H).

Found: C, 71.57; H, 6.57%. Calcd for $C_{13}H_{14}O_3$: C, 69.88; H, 6.84%.

5-*(p-Tolyl)*-5-*methoxy*-2-*oxo*-2,5-*dihdyrofuran (XXI).* ν^{film}: 1810, 1775, 1670, 1610, 1200 and 815 cm^{-1}. $\lambda_{\text{max}}^{\text{EtOH}}$ (ε): 203 (12000), 245 (5200), 263 (4100), 270 (3000) and 276 nm (3400). τ^{CDCl_3}: 2.61 (d, 2H), 2.68 (d, 1H), 2.79 (d, 2H), 3.86 (d, 1H), 6.64 (s, 3H) and 7.62 (s, 3H).

Found: C, 70.40; H, 5.89%. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92%.

A Kinetic Study of the Photoreaction of II. A solution of 250 mg of II in 5 m*l* of methanol was divided among 5 Pyrex tubes. These Pyrex tubes were then irradiated for 8, 24, 48, 72, and 96 hr respectively. The concentrations of III, II, IV, and V in each solution were estimated from the intensity of the NMR signals at τ 3.20 (d, olefinic proton of II), 3.91 (d, α-olefinic proton of III), 5.57 (t, methine proton of IV and V), and 6.26 (s, ester methyl protons of V). The results are plotted in Fig. 2.

The Dark Reaction of II in Methanol. A solution of 50 mg of II in 1 m*l* of methanol was left to stand in a dark place for 24 hr, this gave 12% of VI, which was identified by means of comparison with an authentic sample.

The Thermal Reaction of II in Methanol. A solution of 500 mg of II in 10 m*l* of methanol was refluxed for 24 hr, V and VI were thus obtained in 36 and 64% yields respectively.

The Irradiation of VI in Methanol. By irradiation for 120 hr through a Pyrex filter, a solution of 30 mg of VI in 1 m*l* of methanol gave 87% methyl *cis-β-(p*-ethylbenzoyl)acrylate.

However VI was recovered when the solution was refluxed for 24 hr in methanol.

The Reaction of III in Methanol. When irradiated for 96 hr through a Pyrex filter, or when refluxed for 24 hr, a solution of 30 mg of III in methanol was not changed.

We wish to thank Dr. O. Kikuchi, Department of Chemistry, Tokyo Kyoiku University, for kindly discussion of the calculations with us.