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The Photoreaction of β-Benzoylacrylic Acid

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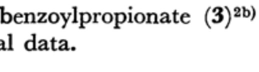
The product of the irradiation of *trans*-β-benzoylacrylic acid (**1**) in methanol was proved to be α-methoxy-β-benzoylpropionic acid (**2**), whose methyl ester was identified with an authentic material. On the other hand, the product of the irradiation of methyl *trans*-β-benzoylacrylate (**5**) was the *cis*-isomer. The photoreaction of **1** in various solvents, including EtOH, *iso*-PrOH, *t*-BuOH, ether, and AcOH, was examined from the standpoints of the *cis-trans* isomerization and alcohol addition. The rate of the photoreaction of **1** in methanol was determined, and a reasonable mechanism for the over-all reaction was proposed.

Only a few studies of β-acyl- and β-aroyl-acrylic acids have been found in the literature.[1] Previously we ourselves reported on the structures and the reactions of these systems.[2] Also, we found three kinds of photoproducts from these systems[3]—that is, *cis-trans* isomers, angelica lactones, and alcohol adducts. Lutz[4] first reported the *cis-trans* isomerization of methyl β-benzoylacrylate under sunlight without any solvent or in benzene. Kropp[5] found that the photoaddition of alcohol to an olefinic double bond was limited to six- or seven-membered cyclic olefins; larger ring or acyclic systems capable of easily undergoing *cis-trans* photoisomerization showed no evidence of adduct formation.

Recently it has been found that methanol, when added to *trans*-β-benzoylacrylic acid (**1**) under the irradiation of UV light, gave β-benzoyl-α-methoxypropionic acid (**2**).[3,6] This is the first example of the photoaddition of methanol to acyclic olefins giving a methoxy derivative except in the case of Stoermer's work, which was reinvestigated by Kropp.[5] However, the formation of no adduct was detected. The present paper will deal with the photoreaction of *trans*-β-benzoylacrylic acid (**1**) in various solvents and will discuss the reaction mechanism.

By the external irradiation of **1** in methanol, **2** was obtained almost quantitatively. The product was methylated by diazomethane. The methyl ester was identified with the authentic methyl α-methoxy-β-benzoylpropionate (**3**)[2b] on the bases of the spectral data.



$$C_6H_5COCH_2\underset{R_1}{\underset{|}{C}}HCOOR_2$$

2 $R_1=OCH_3$, $R_2=H$
3 $R_1=OCH_3$, $R_2=CH_3$

It was confirmed that **2** was not obtained without light under the same conditions. Table 1 shows the results of the reactions of **1** in various solvents. Photoaddition was observed only when methanol or ethanol was used as the solvent. The alcohols with larger alkyl groups, *e.g.*, isopropanol or *t*-butanol, did not add to **1**. In ether, acetic acid, or tetrahydrofuran, or without a solvent, **1** was turned to the *cis*-isomer **4** photochemically. From these results, it is clear that the addition of alcohol becomes difficult as the alkyl group of alcohol becomes bulky.

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[1] For example: a) E. Shaw, *J. Am. Chem. Soc.*, **68**, 2510 (1946); b) R. Scheffold and T. Dubs, *Helv. Chim. Acta*, **50**, 798 (1967); c) N. Hellström, *Nature*, **187**, 146 (1960).

[2] a) N. Sugiyama, T. Gasha, H. Kataoka and C. Kashima, This Bulletin, **41**, 971 (1968); b) N. Sugiyama, T. Gasha, H. Kataoka and C. Kashima, submitted to *J. Chem. Soc.*

[3] N. Sugiyama, H. Kataoka, C. Kashima and K. Yamada, This Bulletin, **41**, 2219 (1968).

[4] R. E. Lutz, *J. Org. Chem.*, **13**, 284 (1948).

[5] P. J. Kropp, *ibid.*, **32**, 3222 (1967).

[6] D. V. Rao, V. Lamberti and H. M. Gardner, *Tetrahedron Letters*, **1968**, 1613.

TABLE 1. PRODUCTS IN VARIOUS SOLVENTS BY THE IRRADIATION OF **1**

Solvent	Time (hr)	Product %	
		cis-isomer	alcohol adduct
none	45	12	
MeOH	12	17	12
MeOH	120		100
EtOH	72		25
i-PrOH	72	40	
t-BuOH	72	47	
Ether	45	20	
AcOH	48	30	
AcOH-MeOH (1 : 1)	48	46	
H_2O-MeOH (2 : 1)	49		20 (OMe)
Ether-MeOH*	72	40	
HCl-MeOH**	72		18
THF	72	55	

* A several drops in 1 *ml* of methanol.

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In order to confirm the structure of the photoproduct, **4**, methyl *cis-β*-benzoylacrylate (**6**)[7] was prepared by the irradiation of methyl *trans-β*-benzoylacrylate (**5**) in methanol. As the spectral data of **6** have not yet been reported, the UV, IR, and NMR spectra of **6** were measured, as will be shown in the Experimental section. All the spectral data strongly support the structure **6**. The IR spectrum of **4** shows the characteristic *cis*-olefinic bands at 1415 cm^{-1} (CH, in-plane), 745, and 695 cm^{-1} (CH, out-of-plane).[8] The NMR spectrum shows a doublet of olefinic protons at τ 2.89 and 3.68, with a coupling constant of 12.0 Hz. These data support the *cis*-configuration of **4**.

Furthermore, in acetic acid - methanol (1 : 1) or in methanol containing a several drops of ether, methanol did not add, but the *cis*-isomer **4** was obtained. In water-methanol (2:1), the adduct **2** was obtained, indicating that methanol addition took place while water addition did not. In a methanol solution containing a few drops of hydrochloric acid, the adduct was formed, but the yield was low. These results, make it probable that the excess acidic proton disturbs the alcohol addition. Methyl *trans-β*-benzoylacrylate **5**, however, did not react with methanol to give the adduct in methanol under irradiation.[3] Therefore, it might be concluded that the presence of a free carboxyl group in **1** is essential for the alcohol addition.

Next, the rate of the formation of products during the irradiation of **1** in methanol was determined, as is shown in Fig. 1. The starting material, **1**, first decreased gradually and then disappeared completely after 5 days. During the course of this period, the adduct **2** gradually increased, while the *cis*-isomer first increased and then gradually decreased.

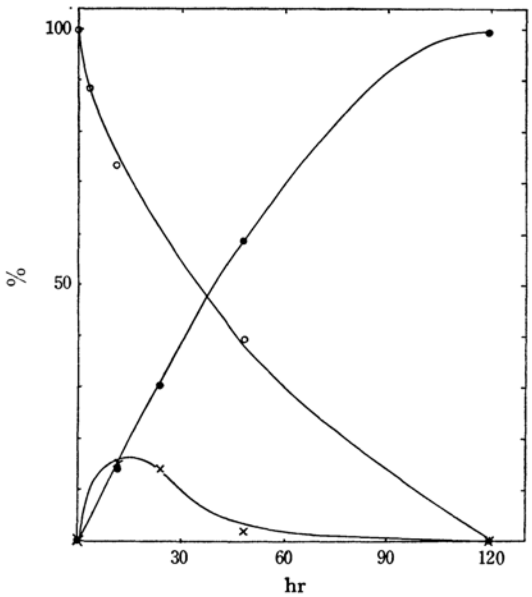
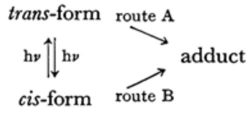


Fig. 1. The rate of the photoreaction of **1** in methanol.

○—○—○ *trans*-form

●—●—● adduct

×—×—× *cis*-form



Scheme 1

From these results, it can be presumed that the adduct **2** will be produced *via* route A or B in Scheme 1. When **1** was irradiated in tetrahydrofuran (THF) for 72 hr, a mixture of *trans*- and *cis*-isomers (45:55) was obtained. When the methanol solution of this mixture was left to stand for 5 days in a dark place at room temperature, the adduct **2** and the *trans*-isomer were obtained in 37% and 63% yields respectively, and the *cis*-isomer was not found. These facts suggest that the *cis*-isomer **4**, formed by photochemical *cis-trans* isomerization, reacted with methanol to give the adduct **2** (route B).

Now let us presume the reaction route shown in Scheme 2. Scheme 2 explains that the free carboxylic acid is essential for the alcohol addition, and that an excess amount of acid disturbs the reaction. Considering that the *cis*-isomer **4** reacted with methanol to give the adduct **2** in a dark place,

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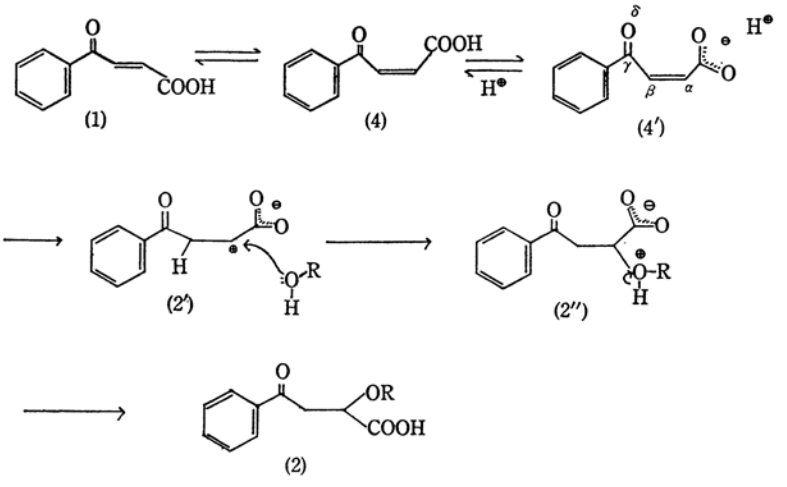
[7] G. P. Rice, *J. Am. Chem. Soc.*, **45**, 222 (1923).

[8] K. Nakanishi, "Infrared Absorption Spectroscopy," Nankodo Co., Ltd., Tokyo (1962), pp. 24, 124, 125.



Scheme 2

the *cis*-acid **4** might be first produced by light and then dissociated to the carboxylate anion **4′**. In the presence of excess acid, the anion **4′** would change to the non-dissociated acid **4**, and the addition could not proceed. This is the reason why the adduct **2** is not obtained in acetic acid, in acetic acid - methanol (1 : 1), or in methanol containing a trace of hydrochloric acid. Moreover, isopropanol or *t*-butanol disturbed the alcohol addition and only *cis-trans* isomerization occurred. This is because the hydroxy oxygen of isopropanol or *t*-butanol is more negative than those of methanol or ethanol because of the inductive effect of the alkyl group. The dissociated proton coordinates to the hydroxy oxygen of alcohol; therefore, the alcohol cannot attack **4′**, as with **2′** or **2″**. Furthermore, the bulkiness of alcohol may also influence an alcohol attacking olefin. The fact that the *cis*-isomer was obtained in methanol containing a small amount of ether can also be explained by a consideration similar to that ether can stabilize the structure **4′**, but as for this point, more detailed experiments are needed.

Experimental

Matrials. ***trans*-β-Benzoylacrylic Acid** (**1**) was prepared by the method of Papa; yellow needles, mp 94—95.5°C (lit. 98—99°C).[9]

UV (λ_{max} nm (ε), in EtOH): 238 (11000), 272 (8900), 357 (86).

Methyl *trans*-β-Benzoylacrylate (**5**) was prepared by the method described in a previous paper,[2)] mp 34°C.

All the solvents were commercially-available Guaranteed Reagents.

Instrumentation. The infrared and ultraviolet spectra were measured on a Hitachi EPI-2-type infrared spectrometer and a Hitachi EPS-3T-type recording spectrometer respectively.

A Taika 500 W high-pressure mercury lamp was used as the irradiation source, while a Pyrex tube was used as the filter and reaction vessel. The NMR spectra were recorded in deuterochloroform, with TMS as the internal standard, with an Hitachi H-60 high-resolution spectrometer.

For paper chromatography we used Toyo Filter Paper No. 53 and *n*-butanol (saturated with a 3% aqeuous ammonia solution).

Irradiation of *trans*-β-Benzoylacrylic Acid (**1**) **in Methanol.** One gram of **1** was dissolved in 20 m*l* of methanol, and then the solution was irradiated for 5 days. The solvent was removed under reduced pressure. It was confirmed by a study of the NMR spectrum that the starting material, **1**, did not remain, and that β-benzoyl-α-methoxypropionic acid (**2**) was formed almost quantitatively as a yellow oil.

NMR (τ, in $CDCl_3$): 1.8—2.7 (m, phenyl), 2.55 (broad s, COOH), 5.55 (t, J=6.0 Hz, α-methine), 6.42 (s, $-OCH_3$), 6.48 (d, J=6.0 Hz, β-methylene).

R_f value of paper chromatography: 0.52 (that of **1**: 0.40).

Crude **2** was methylated with diazomethane to give methyl β-benzoyl-α-methoxypropionate (**3**), which was then purified by silica-gel - column chromatography and eluted with benzene - ethyl acetate (19 : 1), as a yellow liquid.

IR (cm^{-1}, liq. film): 1750 ($COOCH_3$), 1685 (Ar–CO–) 1600 (phenyl), 1195 (C–O–C).

UV (λ_{max} nm (ε), in EtOH): 244 (11000), 280 (1100), 323 (66).

NMR (τ, in $CDCl_3$): 1.82—2.66 (m, phenyl), 5.55 (t, J=6.0 Hz, α-methine), 6.23 (s, $COOCH_3$), 6.52 (s, $-OCH_3$), 6.62 (d, J=6.0 Hz, β-methylene).

3 was identified with an authentic sample[2b)] by means of its IR, UV, and NMR spectra.

Irradiation of Methyl *trans*-β-Benzoylacrylate (**5**) **in Methanol.** A methanol solution of **5** (500 mg/10 m*l*) was irradiated in a Pyrex tube for 5 days, after which the solvent was removed under reduced pressure. The NMR spectrum of this residue showed that 76% of the **5** had changed to methyl *cis*-β-benzoylacrylate

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9) D. Papa, E. Schwenk, F. Villani and E. Klingsberg, *J. Am. Chem. Soc.*, **70**, 3356 (1948).

(**6**). The residue was washed with ice-cooled methanol and recrystallized from methanol. Colorless needles, mp 66°C (lit. 67°C).⁷⁾

IR (cm^{-1}, KBr): 1725 (ester C=O), 1675 (Ar–CO–), 1640 (C=C), 1395 (*cis*-olefin, in-plane), 760, 740, 705 (*cis*-olefin, out-of-plane), 735, 690 (phenyl).

UV (λ_{max} nm (ε), in EtOH): 251 (11800), 280 (sh, 3790), 342 (152).

NMR (τ, in $CDCl_3$): 1.9—2.7 (m, phenyl), 3.13 (d, J=12.0 Hz, olefinic proton), 3.76 (d, J=12.0 Hz, olefinic proton), 6.42 (s, ester methyl).

Irradiation of 1 in Ethanol. An ethanol solution of **1** (250 mg/5 m*l*) was irradiated for 10 days. The subsequent evaporation of the solvent under reduced pressure gave β-benzoyl-α-ethoxypropionic acid (**7**), which was then purified by cellulose-powder chromatography and eluted with *n*-butanol saturated with 3% aqueous ammonia; pale yellow needles, mp *ca.* 93°C.

IR (cm^{-1}, KBr): 2800—2300 (COOH), 1715 (COOH), 1675 (Ar–CO–), 1600 (phenyl), 1260, 1210 (C–O–C), 720, 675 (phenyl).

UV (λ_{max} nm (ε), in EtOH): 244 (9300), 273 (sh, 3400), 345 (200).

NMR (τ, in $CDCl_3$): 1.2 (s, COOH), 1.8—2.7 (m, phenyl), 5.39 (t, J=6.0 Hz, methine), 6.24 (q, J=6.0 Hz, –OEt, methylene), 6.51 (d, J=6.0 Hz, methylene), 8.78 (t, J=6.0 Hz, –OEt, methyl).

β-Benzoyl-α-ethoxypropionic Acid (7). A solution of β-benzoylacrylic acid (1 g) in 30 m*l* of ethanol containing 0.1 m*l* of sulfuric acid was refluxed for 4 hr. The reaction mixture was then diluted with water and extracted with ether. The ethereal layer was washed with a sodium carbonate solution and then with water, and dried with anhydrous sodium sulfate. After the solvent had been removed, ethyl β-benzoyl-α-ethoxypropionate (**8**) was obtained; 0.4 g, yellow liquid.

IR (cm^{-1}, liq. film): 1740 (ester C=O), 1685 (Ar–CO–), 1195 (C–O–C).

UV (λ_{max} nm (ε), in EtOH): 243 (15000).

NMR (τ, in $CDCl_3$): 1.9—2.6 (m, phenyl), 5.45 (t, J=6.0 Hz, methine), 5.75 (q, J=6.0 Hz, ester methylene), 6.25 (q, J=6.0 Hz, ether methylene), 6.65 (d, J=6.0 Hz, methylene), 8.70 (t, J=6.0 Hz, ester methyl), 8.80 (t, J=6.0 Hz, ether methyl).

Found: C, 67.19; H, 7.22%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%.

One hundred milligrams of **8** were dissolved in 10 m*l* of 0.5% ethanolic potassium hydroxide, and then the mixture was stirred for 15 hr at room temperature. After hydrochloric acid had been added to the reaction mixture, it was extracted with ether. From the ether solution β-benzoyl-α-ethoxy-propionic acid (**7**) was obtained. This synthetic sample was found by paper chromatography and the spectral data to be identical with the photoproduct, **7**, of the preceding section.

Irradiation of 1 in Various Solvents. In 1 m*l* of a solvent, 50 mg of **1** were dissolved, and the mixture was irradiated for 2—3 days in a Pyrex tube. After irradiation, the solvent was removed under reduced pressure; the NMR spectrum of the residue was immediately measured, and the yields of the products were calculated from the integration of the spectrum.

The Solution of 1 in Methanol with Time. A solution of **1** (300 mg) in 6 m*l* of methanol was divided into six aliquots, which were then irradiated for 0, 3, 12, 24, 48, and 120 hr respectively. On each aliquot, after the removal of the solvent, the NMR spectrum of the residue was measured at τ 3.17 (d, olefinic proton of **1**), 3.65 (d, olefinic proton of **4**) and 5.55 (t, methine proton of **2**); the yields of **1**, **4** and **2** were calculated from the integration of each signal. The results are plotted in Fig. 1.

The Dark Reaction of a Methanol Solution of the Mixture of *cis*- and *trans*-Isomers of β-Benzoylacrylic Acid. Fifty milligrams of **1** were dissolved in 1 m*l* of THF, and the mixture was irradiated for 72 hr. After the solvent had been removed under reduced pressure, a 55:45 mixture of *cis*- and *trans*-β-benzoylacrylic acid was obtained. This mixture was dissolved in 1 m*l* of methanol and then left to stand for 72 hr at a dark place. The adduct **2** and the *trans*-isomer **1** were obtained in 37% and 63% yields respectively.

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