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The Photoreaction of 1,2-Dibenzoylethylene in Acidic Methanol

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We have previously reported that the photoreaction of β-aroylacrylic acids in methanol produced the methanol adducts, β-aroyl-α-methoxypropionic acids.[1] β-Aroylacrylic acids have the structure of an α,β-unsaturated γ-ketoacid. As an analogy, 1,2-dibenzoylethylene (I), an α,β-unsaturated γ-diketones, is expected to give the methanol adduct upon irradiation. On the other hand, Griffin[2] and Zimmerman[3] reported that the irradiation of I in methanol gave only the rearrangement product, methyl 4-phenyl-4-phenoxy-3-butenoate (II), unlike as in the methanol addition reaction. Thus, it is interesting to re-examine the irradiation of I in methanol.

Results and Discussion

We found that the irradiation of I in methanol gave II as the main product, as well as a methanol adduct, 1,2-dibenzoyl-1-methoxyethane (III), as the minor product. The structure of III was determined by the spectral data and by identification with an authentic sample.[4] The yields

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

[2] G. W. Griffin and E. J. O'Connell, *J. Amer. Chem. Soc.*, **84**, 4148 (1962).

[3] H. E. Zimmerman, H. G. C. Dürr, R. G. Lewis and S. Bram, *ibid.*, **84**, 4149 (1962); H. E. Zimmerman, H. G. Dürr, R. S. Givens and R. G. Lewis, *ibid.*, **89**, 1863 (1967).

[4] R. E. Lutz and C-K. Dien, *J. Org. Chem.*, **21**, 551 (1956).

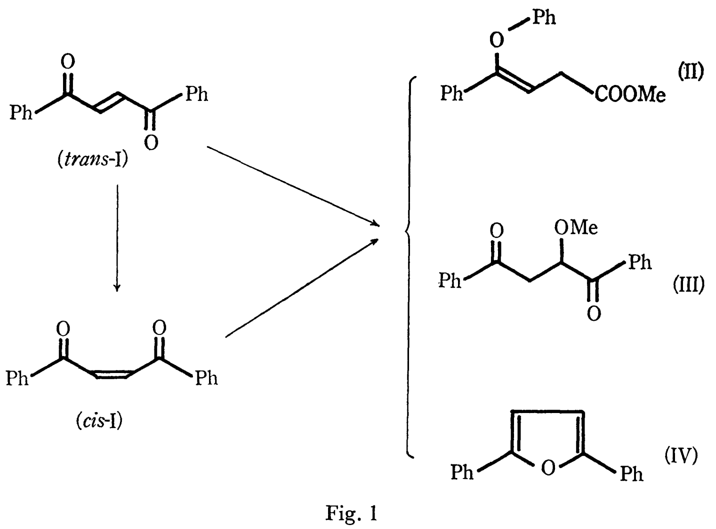

Fig. 1

Table 1. The photoproducts from *trans*-1,2-dibenzoylethylene in acidic methanol

Concn. of HCl mol/*l*	Product Total %	Products		
		II%	III%	IV%
0	68.6	95	5	0
9.9×10^{-6}	79.5	90	10	0
9.5×10^{-5}	70.0	95	5	0
9.9×10^{-5}	77.6	94	4	2
1.9×10^{-4}	57.6	78	19	4
4.7×10^{-4}	45.6	29	47	24
9.5×10^{-4}	52.1	15	56	28
9.9×10^{-4}	49.0	5	40	55

of II and III were estimated by means of the intensity of the NMR signals, which appeared as triplets at δ 6.01 and 5.43 ppm, and which were assigned to the olefinic proton of II and the methine proton of III respectively. The mechanism of the formation of III seems to be similar to that of the photoaddition of β-benzoylacrylic acids.

Considering that the addition of methanol to β-benzoylacrylic acids was initiated by protonation on carbonyl oxygen,[5] the yield of III from I was expected to increase in acidic methanol. Thus, the photoreaction of I was examined in methanol containing various amounts of hydrochloric acid. As is shown in Table 1, when the concentration of hydrochloric acid was 9.9×10^{-5} mol/*l* or less, the

Table 2. The photoproducts from *trans*- or *cis*-1,2-dibenzoylethylene in methanol or in acidic methanol

Structure of I	Concn. of HCl (mol/*l*)	Filter	Total product %	Products		
				II%	III%	IV%
trans	0	Py$^{a)}$	68.6	95	5	0
trans	0	Py+Ni$^{b)}$	13.2	100	0	0
trans	0	Py+Cu$^{c)}$	90.6	100	0	0
cis	0	Py$^{a)}$	57.1	100	0	0
cis	0	Py+Ni$^{b)}$	26.7	100	0	0
cis	0	Py+Cu$^{c)}$	85.1	100	0	0
trans	4.7×10^{-4}	Py$^{a)}$	45.6	29	47	24
trans	4.7×10^{-4}	Py+Ni$^{b)}$	30.1	18	73	9
trans	4.7×10^{-4}	Py+Cu$^{c)}$	69.2	33	47	21
cis	4.7×10^{-4}	Py$^{a)}$	51.4	49	49	3
cis	4.7×10^{-4}	Py+Ni$^{b)}$	21.1	25	75	0
cis	4.7×10^{-4}	Py+Cu$^{c)}$	68.6	26	65	10

a) Pyrex filter.
b) Pyrex filter and aqueous solution filter of $NiSO_4$ and $CoSO_4$.
c) Pyrex filter and aqueous solution filter of $CuSO_4$ and NH_4OH.

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[5] C. Kashima, H. Kataoka, K. Tanaka and N. Sugiyama, This Bulletin, **43**, 1473 (1970).

effect of the acid was not observed in the photoreaction of I. At more than 1.9×10^{-4} mol/*l*, the yield of II decreased and that of III increased.

Moreover, in methanol containing more than 1.9×10^{-4} mol/*l* of hydrochloric acid, 2,5-diphenylfuran (IV) was obtained as one of the photoproducts. The structure of IV was determined by the spectral data and by identification with an authentic sample.[6] The yield of IV was estimated by means of the singlet signal of the NMR spectrum at δ 6.68 ppm assigned to two methine protons on the furan ring. In the presence of 4.7×10^{-4} mol/*l* of hydrochloric acid in methanol, the reaction mixture was shown to contain 29% of II, 47% of III, and 24% of IV. Then, the influence of the light source on the photoreaction of I was examined (Table 2). In the absence of acid, the main product is II, even when the light is filtered through an aqueous solution of nickel sulfate and a cobalt sulfate mixture or ammoniac copper sulfate. However, in the presence of 4.7×10^{-4} mol/*l* of acid, the yield of III increased when the light came through a filter of nickel sulfate and a cobalt sulfate solution. In acidic methanol, *cis*-1,2-dibenzoylethylene also gave II and III photoproducts.

TABLE 3. THE PHOTOPRODUCTS FROM *trans*-1,2-DIBENZOYLETHYLENE IN ACIDIC ALCOHOLS (5×10^{-4} mol/*l* HCl)

Alcohol	Total product %	Rearrangement product %	Alcohol adduct %	Diphenyl furan %
MeOH	70.4	29	52	19
EtOH	67.4	80	20	0
n-PrOH	53.9	75	25	0
iso-PrOH	30.8	100	0	0
t-BuOH	36.8	100	0	0

Furthermore, the photoreaction of I in alcohols other than methanol was examined in the presence of 5×10^{-4} mol/*l* of hydrochloric acid; the results are listed in Table 3. In ethanol or *n*-propanol, both the alcohol adduct and the rearrangement product were obtained, but in the sterically-hindered alcohols, such as isopropanol or *t*-butanol, only the rearrangement product was obtained. In case of alcohols other than methanol, IV was not obtained.

By the facts that the addition occurs by the irradiation in acidic methanol or ethanol, and that the *cis* isomer gives the addition product in acidic methanol, it can be deduced that the mechanism of this reaction is similar to that of the photoaddition of methanol to β-benzoylacrylic acids.[1,5]

Experimental

Materials. *trans*-1,2-Dibenzoylethylene was prepared from fumaroyl chloride by a Friedel-Crafts reaction and was recrystallized from ethanol; mp 110.5°C (lit,[7] 109—110°C). λ^{EtOH} (ε): 268 (18400) and 360 nm (sh, 257). δ^{CDCl_3}: 7.97 (s, 2H), 7.9—8.15 (m, 6H) and 7.4—7.7 ppm (m, 4H). *cis*-1,2-Dibenzoylethylene was prepared by the irradiation of I in ethanol;[8] mp 135.5°C. λ^{EtOH} (ε): 260 (17800) and 340 nm (sh, 210). δ^{CDCl_3}: 7.16 (s, 2H), 7.4—7.7 (m, 6H) and 7.8—8.1 ppm (m, 4H).

Instrumentation. The infrared and ultraviolet spectra were measured with a Hitachi EPI-2-type infrared spectrometer and a Hitachi EPS-3T-type spectrometer respectively. The NMR spectra were recorded with a Hitachi H-60 high-resolution NMR spectrometer, with TMS as the internal standard. An Ushio 450 W high-pressure mercury lamp was used as the irradiation source.

Filter. The light from the high-pressure mercury lamp was filtered by three types of filters:

1) Pyrex filter; transparent at wavelengths longer than 310 nm.

2) Aqueous solution (3 *l*) of nickel sulfate (1350 g) and cobalt sulfate (320 g) and a Pyrex filter; thickness 1 cm; transparent from 290 to 370 nm; 290 nm, 5% T; 310 nm, 50% T; 330 nm, 70% T; 350 nm, 25% T; with a maximum at 320 nm, 85% T.

3) Aqueous solution (2 *l*) of copper sulfate (100 g) and aqueous ammonia (400 m*l*); thickness 1 cm; transparent from 320 to 480 nm; 330 nm, 15% T; 350 nm, 47% T; 370 nm, 68% T; 390 nm, 80% T; 410 nm, 82% T; 430 nm, 69% T; 450 nm, 40% T; 470 nm, 8% T; with a maximum at 404 nm, 82.5% T.

Irradiation of I. A solution of 100 mg of I in 5 m*l* of the methanol was irradiated at room temperature. After the solvent had been removed, the residue was analyzed by means of the intensity of the NMR signals at δ 5.43 (t, methine proton of III), 6.01 (t, olefinic proton of II), and 6.68 ppm (s, methine protons of IV). The residue was chromatographed on a silica-gel (Merck 7734) column with a benzene-ethyl acetate mixture, we thus obtained II, III, and IV in a pure state.

Methyl 4-Phenyl-4-phenoxy-3-butenoate (II). ν^{film}: 1735, 1600, 1485, 1220, 750 and 690 cm^{-1}. δ^{CDCl_3}: 3.26 (d, 2H), 3.60 (s, 3H), 6.01 (t, 1H) and 6.7—7.6 ppm (m, 10H).

1,2-Dibenzoyl-1-methoxyethane (III). ν^{film}: 1680, 1595, 1450, 1110, 1090, 755 and 685 cm^{-1}. δ^{CDCl_3}: 3.37 (s, 3H), 3.41 (d, 2H), 5.43 (t, 1H), 7.2—7.6 (m, 6H) and 7.8—8.2 ppm (m, 4H).

2,5-Diphenylfuran (IV). mp 85°C. ν^{KBr}: 1600, 1020, 920, 910, 795, 760 and 690 cm^{-1}. δ^{CDCl_3}: 6.68 (s, 2H) and 7.1—7.9 ppm (m, 10H).

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[8] H. Keller, R. Pasternak and H. V. Halban, *Helv. Chim. Acta*, **29**, 512 (1946).