

The Photoreaction of β -Acyl- and β -Aroyl-acrylic Acids

Noboru SUGIYAMA, Hiroshi KATAOKA and Choji KASHIMA

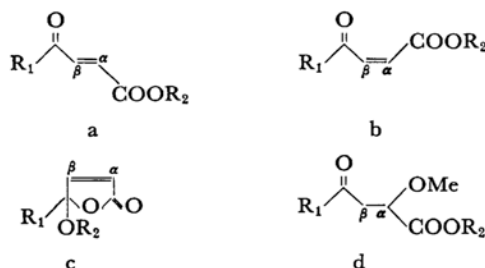
Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo

and Kazutoshi YAMADA

Department of Synthetic Chemistry, Chiba University, Yayoi-cho, Chiba

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During the course of an investigation of the reaction of β -acyl- and β -aroyl-acrylic acids,^{1,2} we have found that the methanol adduct, β -benzoyl- α -methoxypropionic acid (1d),³ and *cis*- β -benzoylacrylic acid (1b) were obtained from *trans*- β -benzoylacrylic acid (1a) by irradiation in methanol.*¹ We have studied the photoreaction of 1a in various solvents as well as the analogous photoreactions of β -acyl- and β -aroyl-acrylic acids and their esters (2a—8a).



- 1) $R_1 = \text{Ph}$ $R_2 = \text{H}$; 2) $R_1 = \text{Ph}$, $R_2 = \text{Me}$;
- 3) $R_1 = p\text{-MeC}_6\text{H}_4$, $R_2 = \text{H}$;
- 4) $R_1 = p\text{-MeOC}_6\text{H}_4$, $R_2 = \text{H}$;
- 5) $R_1 = p\text{-BrC}_6\text{H}_4$, $R_2 = \text{H}$;
- 6) $R_1 = \text{Me}$, $R_2 = \text{H}$; 7) $R_1 = R_2 = \text{Me}$;
- 8) $R_1 = t\text{-Bu}$, $R_2 = \text{H}$

Following three types of reaction were observed in the photoreaction listed in Table 1. a \rightarrow b: *trans* to *cis* isomerization. a \rightarrow c: isomerization to angelica lactones. a \rightarrow d: alcohol addition to the olefinic double bond.

These reactions occurred complicatedly. For example, compound 1a in ether exclusively afforded the *cis*-isomer 1b, whereas that in methanol gave two products, the *cis*-isomer 1b and methanol adduct 1d. On the other hand, the irradiation of the methanol solution of 3a gave rise to both 3c and 3d. A methanol solution of 6a and 8a produced only the angelica lactone type compounds 6c and 8c. The details of these photoreactions will be reported elsewhere.

TABLE 1. PHOTOREACTION PRODUCTS OF β -ACYL- AND β -AROYL-ACRYLIC ACIDS

Compd.	Solv.	Time (hr)	Product (%)		
			b	c	d
1a	no	45	12	0	0
1a	MeOH	12	17	0	14
1a	MeOH	120	0	0	100 ^a
1a	EtOH	72	0	0	25
1a	ether	45	20	0	0
2a	MeOH	17	90	0	0
3a	MeOH	120	0	23 ^b	77 ^c
4a	MeOH	1 week	18	0	82 ^a
5a	MeOH	72	0	4 ^b	88 ^c
6a	no	44	0	80	0
6a	MeOH	45	0	85	0
7a	no	1 week	90	0	0
7a	acetone	17	78	0	0
8a	MeOH	31	0	100	0

a) Type d products (1d and 4d) were obtained as free acids ($R_2 = \text{H}$), which were esterified with diazomethane and subjected to NMR analysis. The methyl ester of 1d was also identified by comparison with authentic sample.²

b), c) Irradiation gave directly methyl esters and methyl ethers.

TABLE 2. THE NMR DATA (τ) OF α AND β PROTONS OF STARTING MATERIALS AND PRODUCTS

	a	b	c	d
1	2.04, 3.17	2.89, 3.68	—	5.55, 6.50
2	2.02, 3.12	3.13, 3.76	—	—
3	2.04, 3.17	3.76	2.68, 3.86	5.52, 6.59
4	2.01, 3.17	2.84, 3.60	—	5.55, 6.63
5	2.14, 3.26	—	3.77*	5.55, 6.63
6	3.20	—	2.84, 3.95	—
7	3.29	3.84	—	—
8	2.37, 3.24	—	2.62, 3.84	—

* $R_2 = \text{Me}$

3) This photoaddition of methanol was reported independently by D. B. Rao *et al.* in *Tetrahedron Letters*, p. 1613 in 1968.

*¹ Taika 500 W high pressure mercury lamp was used as a light source and pyrex tube as a filter.

1) N. Sugiyama, T. Gasha, H. Kataoka and C. Kashima, *This Bulletin*, **41**, 971 (1968).

2) N. Sugiyama, T. Gasha, H. Kataoka and C. Kashima, *J. Chem. Soc.*, in press.