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Photochemistry of β-Acylacrylic Acids and Their Esters

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The irradiation of methyl *trans*-β-acetylacrylate (I-A) in methanol or acetone or without any solvent gave the *cis*-isomer (I-B). On the contrary, the irradiation of the free acid of I-A, *trans*-β-acetylacrylic acid (II-A), in methanol or without any solvent gave the angelica lactone, 5-methyl-5-hydroxy-2-oxo-2,5-dihydrofuran (II-C). The irradiation of *trans*-β-pivaloylacrylic acid (III-A) in methanol also afforded the angelica lactone, 5-*t*-butyl-5-hydroxy-2-oxo-2,5-dihydrofuran (III-C). The reaction route from a *cis*-isomer to an angelica lactone was explained in terms of the inductive effect.

In a previous report of this series[1] three isomeric forms of β-acylacrylic acid, the *trans* form, the *cis* form, and the angelica lactone form, were described. We also found that, on irradiation in ether, *trans*-β-benzoylacrylic acid was isomerized to the *cis* form, while in methanol the methanol addition product, β-benzoyl-α-methoxypropionic acid, was obtained.[2-4] Similarly, β-(*p*-toluoyl)-, β-(*p*-anisoyl)- and β-(*p*-bromobenzoyl)-acrylic acids were found to give the methanol adduct.[5] On the other hand, an angelica lactone was obtained as a by-product of the irradiation of β-(*p*-toluoyl)-acrylic acid. Therefore, three reactions are possible in the irradiation of β-aroylacrylic acids: *cis-trans* isomerization, methanol addition, and lactonization.

1) N. Sugiyama, T. Gasha, H. Kataoka and C. Kashima, This Bulletin, **41**, 971 (1968).
2) N. Sugiyama, H. Kataoka, C. Kashima and K. Yamada, *ibid.*, **41**, 2219 (1968).
3) N. Sugiyama, H. Kataoka, C. Kashima and K. Yamada, *ibid.*, submitted for publication.
4) D. V. Rao, V. Lamberti and H. M. Gardner, *Tetrahedron Letters*, **1968**, 1613.
5) Unpublished data.

It seemed of interest to examine the irradiation of methyl *trans-β*-acetylacrylate (I-A), *trans-β*-acetylacrylic acid (II-A), and *trans-β*-pivaloylacrylic acid (III-A).

Methyl *trans-β*-acetylacrylate (I-A) was irradiated in methanol by a high-pressure mercury lamp for 17 hr at room temperature. The structure of the product was determined to be methyl *cis-β*-acetylacrylate (I-B) as follows. New NMR signals observed as an AB quartet at τ 3.84 (J=12.0 c/s) can be assigned to the *cis* olefinic protons, while the two singlet signals at τ 6.27 and 7.72 represent ester methyl and acetyl methyl protons respectively. The yield of the *cis* isomer was 80%. In the reaction mixture, α-methoxylevulinate[6] was not detected.

Methyl *trans-β*-acetylacrylate (I-A) was also irradiated in a solid state and in an acetone solution under the same conditions as have been described above. In a solid state, I-A gradually turned to a liquid. The product in either a solid state or acetone was identified with its *cis*-isomer by means of the NMR spectra as well as by thin-layer chromatography. The yields were 64% in a solid state and 78% in acetone. When the solid state irradiation was continued for a week, no reaction proceeded except the formation of the *cis*-isomer in a yield of 90%.

The methanol solution of *trans-β*-acetylacrylic acid (II-A) was irradiated for 45 hr at room temperature. The photoproduct shows the carbonyl bands at 1760 and 1740 cm^{-1} in the IR spectrum. The NMR spectrum shows the singlet of methyl protons at τ 8.24 and two doublet signals of olefinic protons at τ 2.74 and 3.92 with a coupling constant of 6.0 c/s. These data suggest that the photoproduct is the angelica lactone of II-A, 5-methyl-5-hydroxy-2-oxo-2,5-dihydrofuran (II-C), which is also obtained from II-A by the treatment of thionyl chloride, followed by alkaline hydrolysis.[7]

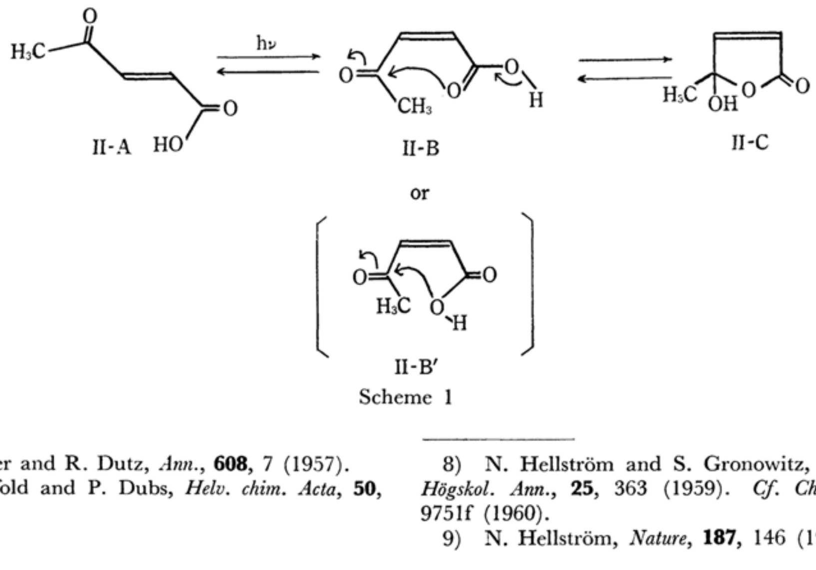
The most conspicuous feature of NMR data is that the signals of the olefinic protons of methyl *cis-β*-acetylacrylate (I-B) appear in an AB quartet at τ 3.87 with a coupling constant 12.0 c/s, while that of methyl α-methoxylevulinate appears at τ 5.55 with a coupling constant of 6.0 c/s, while no signals of *cis*-isomer or of the methanol adduct are observed in this region. The yield of II-C was calculated for 60% based on the signal intensities of II-A and II-C at τ 3.40 and 3.92 respectively.

When the irradiation of II-A was continued for 115 hr, the yield of II-C reached 85%, while no other products were detected except II-A. This yield is reasonable because II-C is unstable, as has been reported by Scheffold,[7] and so about 15% of II-C might return to II-A.

When II-A was irradiated in a solid state, only II-C was obtained. The yield was 32%.

All the *β*-acylacrylic acids generally exist in the *trans* form at room temperature except for maleinaldehydic acid, which favors the angelica lactone form.[8] Considering the fact that methyl *trans-β*-acetylacrylate (I-A) is isomerized to the *cis* form I-B by the irradiation, the *trans* form of II-A is expected to isomerized first into *cis-β*-acetylacrylic acid (II-B). The *cis* acid II-B is expected to cyclize easily to the angelica lactone II-C, for the acid carbonyl is close to the acetyl carbonyl and the dissociated proton can attack acetyl carbonyl as is shown in Scheme 1.

If the acetyl group of II-A is replaced by the bulky pivaloyl group, the keto carbonyl group will be inaccessible to the carboxyl group because of the steric hindrance of the pivaloyl group. Thus, the irradiation of *trans-β*-pivaloylacrylic acid (III-A) was examined. A methanol solution of *trans-β*-pivaloylacrylic acid (III-A)[9] was irradiated for



II-A II-B II-C

II-B′

Scheme 1

6) L. Birkofer and R. Dutz, *Ann.*, **608**, 7 (1957).
7) R. Scheffold and P. Dubs, *Helv. chim. Acta*, **50**, 798 (1967).
8) N. Hellström and S. Gronowitz, *Kgl. Lantbruks-Högskol. Ann.*, **25**, 363 (1959). *Cf. Chem. Abstr.*, **54**, 9751f (1960).
9) N. Hellström, *Nature*, **187**, 146 (1960).

55 hr at room temperature. The photoproduct shows the singals characteristic of the angelica lactone, but no signals characteristic of the *cis* form, the methanol adduct, or the starting material, III-A. The angelica lactone III-C was obtained almost quantitatively. The structure of the angelica lactone, 5-*t*-butyl-5-hydroxy-2-oxo-2,5-dihydrofuran (III-C), was confirmed as follows. The IR spectrum shows the lactone carbonyl bands at 1765 and 1740 cm^{-1}, and the olefinic band at 1610 cm^{-1}. The UV spectrum shows the absorption maximum at 204 nm. In the NMR spectrum, the singlet signal of the *t*-butyl group appears at τ 8.96, and the singlet signal of the hydroxyl proton appears at τ 5.15. The two doublet signals at τ 2.62 and 3.84, which were assigned to olefinic protons (J= 6.0 c/s).

These results make it clear that the steric hindrance does not influence the cyclization step, and that the +I effect is more important. This conclusion is also consistent with the fact that β-adamantoylacrylic acid is cyclized to lactone by the irradiation.[10]

Experimental

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

The NMR spectra were recorded in deuterochloroform, with TMS as the internal standard with a Hitachi H-60-type high-resolution nuclear spectrometer.

A Taika 500 W high-pressure mercury lamp was used as the irradiation source, and a Pyrex tube was used as a filter and also as a reaction vessel.

Materials. *trans-β-Acetylacrylic acid (II-A)* was prepared by the method previously reported;[11] mp 125—126°C (lit. 126°C).[11]

Methyl trans-β-acetylacrylate (I-A) was prepared by the method of Pauly;[12] mp 58.5—60°C (lit. 60°C).[12]

trans-β-Pivaloylacrylic acid (III-A) was prepared by the method of Hellström;[9] mp 68—86°C (lit. 70—92°C).[9]

Irradiation of Methyl *trans-β*-Acetylacrylate (I-A). *A) In Methanol.* One hundred milligrams of methyl *trans-β*-acetylacrylate (I-A) were dissolved in 2 m*l* of methanol, after which the mixture was irradiated for 48 hr at room temperature. After the solvent had been removed methyl *cis-β*-acetylacrylate (I-B) was isolated by silica-gel column chromatography and eluted as a yellow oil with benzene. Yield, 80%.

IR (cm^{-1}, liq. film): 1730 (νC=O, ester), 1695 (νC=O, Ac), 1640 (νC=C), 1380, 900, 800 (δCH).

UV (λ_{max}, in EtOH): end absorption.

Found: C, 60.50; H, 7.70%. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75%.

The formation of the methanol adduct, methyl α-methoxylevulinate, was checked by comparing it with an authentic sample which had been synthesized from II-A by treatment with methanol in the presence of sulfuric acid.[6] Neither a study of the NMR spectra nor thin-layer chromatography could detect the adduct.

B) In Acetone. Fifty milligrams of I-A were dissolved in 1 m*l* of acetone, and the mixture was irradiated for 17 hr. Immediately after the solvent had been removed, the NMR spectrum was measured; the yield of I-B was 78%.

C) Without the Solvents. Fifty milligrams of I-A were dissolved in methanol; the solvent was then removed under reduced pressure, and I-A was fixed on the wall of the Pyrex tube. This solid-state I-A was irradiated for 17 hr at room temperature. The reaction mixture was dissolved in deuterochloroform and was measured on a NMR spectrum. I-B was produced in a 64% yield. When the irradiation continued for 1 week, the yield of I-B was raised to 90%.

Irradiation of *trans-β*-Acetylacrylic Acid (II-A). A methanol solution of *trans-β*-acetylacrylic acid (II-A) (500 mg/10 m*l*) was irradiated for 45 hr at room temperature. 5-Methyl-5-hydroxy-2-oxo-2,5-dihydrofuran (II-C) was then obtained as colorless needles from benzene - methanol (10 : 1). Mp 121—124°C (lit. 126°C);[7] yield, 60%. II-C was identified with an authentic sample.[7]

IR (cm^{-1}, KBr): 3500 (νOH), 1770, 1740 (νC=O, angelica lactone), 1650 (νC=C).

UV (λ_{max} nm(ε), in EtOH): 206 (28900).

NMR (τ, in $CDCl_3$): 2.74 (d, J=6.0 c/s, β-olefinic proton), 3.92 (d, J=6.0 c/s, α-olefinic proton), 4.42 (s, hydroxy proton), 8.24 (s, methyl).

When the irradiation was continued for 1 week, the yield of II-C was 85%, while when II-A was irradiated in the solid state for 112 hr, the yield of II-C was only 32%.

Irradiation of *trans-β*-Pivaloylacrylic Acid (III-A). Sixty milligrams of *trans-β*-pivaloylacrylic acid (III-A) were dissolved in 1 m*l* of methanol, after which the mixture was irradiated for 55 hr at room temperature. After removing the solvent, the residue was recrystallized from ether-benzene. 5-*t*-Butyl-5-hydroxy-2-oxo-2,5-dihydrofuran (III-C) was obtained almost quantitatively, as colorless needles; mp 72—74°C.

IR (cm^{-1}, KBr): 3380 (νOH), 1765, 1740 (νC=O, angelica lactone), 1610 (νC=C).

UV (λ_{max} nm(ε), in EtOH): 204 (18600)..

NMR (τ, in $CDCl_3$): 2.62 (d, J=6.0 c/s, β-olefinic proton), 3.84 (d, J=6.0 c/s, α-olefinic proton), 5.15 (broad s, OH), 8.96 (s, *t*-butyl).

Found: C, 60.52; H, 7.70%. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75%.

10) M. Kuchar, *Collection Czech. Chem. Commun.*, **33**, 880 (1968).

11) L. Wolff, *Ann.*, **264**, 246 (1891).

12) H. Pauly, R. Gilmour and G. Will, *ibid.*, **403**, 119 (1914).