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The Photoreaction of 3-Hexene-2,5-dione in Methanol

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We have investigated the photoreactions of α,β-unsaturated γ-dicarbonyl compounds, such as 1,2-dibenzoylethylene,[1] β-aroylacrylic acids,[2,3] β-acylacrylic acids,[4] and their esters. The photoproducts of these systems in methanol are the *cis* isomers, 4-hydroxy- and 4-methoxy angelica lactones, and methanol adducts. As a part of these investigations, we have now examined the photoreaction of 3-hexene-2,5-dione, one of the α,β-unsaturated γ-diketones, in methanol.

Results and Discussion

By the irradiation of a filtered light through a Pyrex filter in methanol for 6 hr, *trans*-3-hexene-2,5-dione (I), which shows absorption maxima at 228 (ε 14000) and 331 mμ (ε 69), gave the *cis* isomer (II). The structure of II was deduced by means of the spectral data and by identification with an authentic sample.[5] Upon continuous irradiation for 22 hr, I gave two products, III and IV, which were separated by vapor-phase chromatography. In the NMR spectra, III showed singlet signals at δ 5.78, 3.20, and 1.40 ppm, while IV showed them at δ 5.77, 3.10, and 1.48 ppm. From these results and from other spectral and elemental analysis data, the structures of III and IV were deduced to be *cis*- and *trans*-2,5-dimethoxy-2,5-dimethyl-2,5-dihydrofuran respectively. Although the stereo isomers were not separated, the preparation of 2,5-dimethoxy-2,5-dimethyl-2,5-dihydrofuran from 2,5-dimethylfuran has been reported by Levisalles.[5] Thus, we also prepared III and IV by the method of Levisalles, and identified them with the photoproducts.

For the purpose of clarifying the reaction mechanism from I to II, III, and IV, kinetic studies were carried out. The concentrations of I, II, III, and IV in the reaction mixture were measured by means of the NMR spectra and by vapor-phase chromatography. The changes in the concentration with the time are shown in Fig. 1. The curve for II showed a maximum at 5 hr, and those for III and IV, a gradual increase. Also, it was confirmed

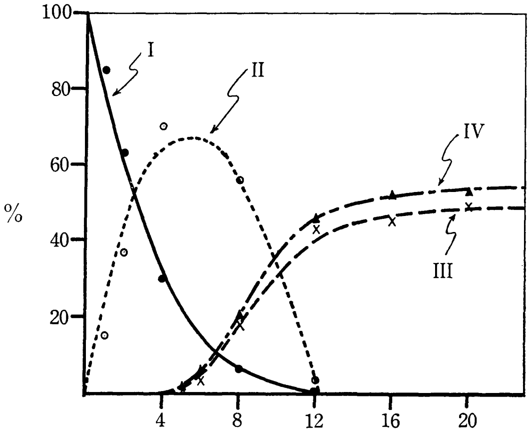

Fig. 1

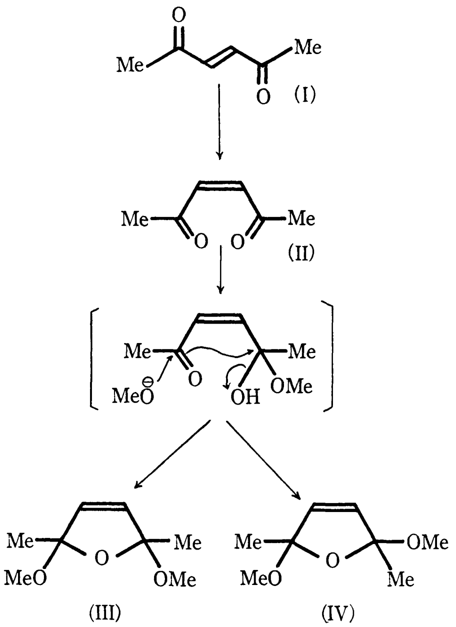

Fig. 2

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[1] C. Kashima and N. Sugiyama, This Bulletin, **43**, 1875 (1970).

[2] N. Sugiyama, H. Kataoka, C. Kashima and K. Yamada, *ibid.*, **42**, 1353 (1969).

[3] C. Kashima, H. Kataoka, K. Tanaka and N. Sugiyama, *ibid.*, **43**, 1473 (1970).

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

[5] J. Levisalles, *Bull. Soc. Chim. Fr.*, (**5**) **24**, 997 (1957).

that II does not react with methanol at room temperature without irradiation.

Thus, a probable reaction mechanism for the formation of III and IV from I may be proposed (Fig. 2). That is, I is isomerized to II, the excited species of which is attacked by methanol to produce the hemiacetal intermediate. This intermediate is immediately cyclized to III and IV in parallel.

From these results, it seems that the photoreaction from I to III and IV is similar to the formation of 4-methoxy angelica lactone.

Experimental

Material. *trans*-3-Hexene-2,5-dione was prepared from 2,5-hexanedione by oxidation with selenium dioxide, and then recrystallized from *n*-hexane; mp 73°C (lit,[6] 78°C). λ^{EtOH} (ε): 228 (14000) and 331 mμ (69). $\delta^{\mathrm{CDCl_3}}$: 6.78 (s, 2H) and 2.38 ppm (s, 6H).

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 A-60 high-resolution NMR spectrometer, with TMS as the internal standard. A Hitachi KGL-2A-type gas-chromatograph analyzer was used with 10% PEG-adipate at 104°C. The light from a Ushio 450-W high-pressure mercury lamp was irradiated on the sample through the Pyrex filter.

***cis*-3-Hexene-2,5-dione (II).** A solution of 100 mg of I in 5 m*l* of methanol was irradiated at room temperature. After 2 hr, the solvent was removed; we then measured the spectra and chromatographed them on a silica-gel thin layer. λ^{EtOH} (ε): 224 mμ (8600). ν^{KBr}: 1675, 1610, 1415, 1390, 1355, 1255, 1215, 1170 and 985 cm^{-1}. $\delta^{\mathrm{CDCl_3}}$: 6.30 (s, 2H) and 2.29 ppm (s, 6H).

The photoproduct was identified with the *cis*-3-hexene-2,5-dione prepared from 2,5-dimethoxy-2,5-dimethyl-2,5-dihydrofuran.[5]

***trans*- and *cis*-2,5-Dimethoxy-2,5-dimethyl-2,5-dihydrofuran (III and IV).** A methanol solution of I was irradiated for 22 hr, and then the solvent was removed. The residual oil was passed through preparative vaporphase chromatography. The first fraction, with Rt 9.5 min, was collected as III. λ^{EtOH} (ε): 251 mμ (342). ν^{film}: 1450, 1370, 1350, 1285, 1170, 1125, 1090, 1050, 945, 890 and 770 cm^{-1}. $\delta^{\mathrm{CDCl_3}}$: 5.78 (s, 2H), 3.20 (s, 6H) and 1.40 ppm (s, 6H).

Found: C, 60.59; H, 9.17%. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92%. The second fraction, with Rt 12.0 min, was collected as IV. λ^{EtOH} (ε): 224 (sh, 179) and 253 mμ (sh, 104). ν^{film}: 1450, 1370, 1350, 1170, 1095, 1050, 945, 890 and 770 cm^{-1}. $\delta^{\mathrm{CDCl_3}}$: 5.76 (s, 2H), 3.10 (s, 6H) and 1.48 ppm (s, 6H).

Found: C, 60.36; H, 8.89%. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92%. Both III and IV were identical with the mixture of *trans*- and *cis*-2,5-dimethoxy-2,5-dimethyl-2,5-dihydrofuran previously prepared from 2,5-dimethylfuran[5] by vapor-phase chromatography.

Kinetic Studies. A solution of 1 g of I in 50 m*l* of methanol was divided into 10 aliquots, which were irradiated at 30°C for 1, 2, 4, 5, 6, 8, 12, 16, 20, and 22 hr, respectively. Each portion was then concentrated, and the concentrations of I, II, III and IV were measured by means of intensity of the NMR signals at δ 6.78 (s, olefinic protons of I) and 6.30 ppm (s, olefinic protons of II), and by means of those of a vapor-phase chromatogram at Rt 9.5 min (III) and 12.0 min (IV).

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6) M. W. Goldberg and P. Müller, *Helv. Chim. Acta*, **21**, 1699 (1938).