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Synthetic Photochemistry. L.[1] Isolation and the X-Ray Structure Determination of Photocyclodimers Formed by UV-Light Irradiation of Alkyl 2,4-Dioxopentanoates

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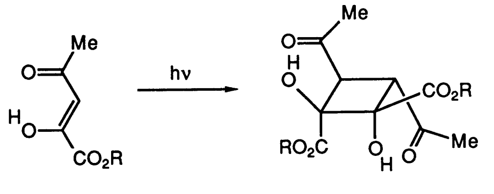
Synopsis. Upon UV-light irradiation with a high-pressure mercury lamp, methyl 2,4-dioxopentanoate in a mixture of benzene and cyclohexane afforded a crystalline head-to-head-[2+2]cyclodimer. Its structure was elucidated by a single-crystal X-ray analysis, as well as ^{1}H and ^{13}C NMR spectroscopy. Ethyl 2,4-dioxopentanoate also gave a cyclodimer.

The de Mayo reaction[2] has been regarded as one of the most synthetically useful photocycloaddition reactions. Among the previously-studied β-diketone photocycloaddends, alkyl 2,4-dioxoalkanoates,[3] being fully enolized in various solvents, have a characteristic reactivity to form regiospecific [2+2]cycloadducts with conjugated olefins, and to give useful intermediates for natural product syntheses.[4] Herein, we wish to report the isolation and structure determination of head-to-head-[2+2]dimers.

When methyl 2,4-dioxopentanoate (**1a**) was irradiated by means of a 400-W high-pressure mercury lamp through a Pyrex glass filter in a mixture of benzene and cyclohexane, a colorless crystalline product (**2a**) was formed and isolated by filtration. Its mass spectrum indicated its molecular composition to be dimeric, and the ^{1}H and ^{13}C NMR strongly suggested the presence of a symmetry element in the molecule. Presumably, **2a** is, therefore, a [2+2]cyclodimer. From the mechanism of photoaddition, the cis relationship for the acetyl and hydroxy groups was expected,[5,6] though the syn- or anti-stereochemistry could not be determined. Unfortunately, spectroscopic differentiation at this point failed; i.e., an ^{1}H NMR satellite band due to the ^{13}C–H coupling could not be detected, or an attempt to measure lanthanoid-induced chemical shift change caused a decompostion of **2a**.



1a R=Me
b R=Et

2a R=Me
b R=Et

Scheme 1.

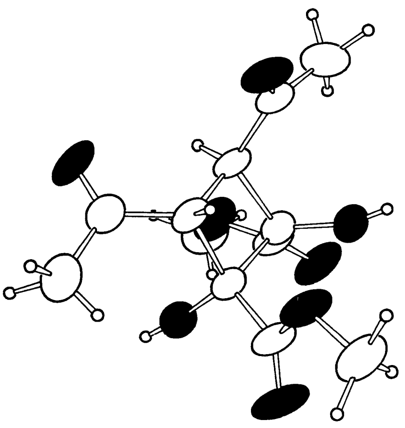


Fig. 1. The ORTEP drawing of **2a**. Dark atoms denote the oxygen atoms.

Therefore, an X-ray structure analysis with a single crystal of **2a** was carried out (see Experimental): The molecular structure obtained by the analysis was displayed as a computer-generated drawing (Fig. 1).

Similar irradiation of ethyl 2,4-dioxopentanoate (**1b**) gave a homologous cyclodimer (**2b**) in 10% yield. From the ^{1}H NMR spectral similarity it is certain that **2b** and **2a** have the same stereochemistry.

Previously, no dimer of free enolized β-diketones have been detected, although a cyclodimer of dehydroacetic acid reacted at the β-acyloxy enone moiety.[7] This is particularly interesting since none of the protophotoadducts from ordinary 2,4-diketoalkanes with olefins has been known. On the other hand, from the 2,4-dioxoalkanoates, several proto-cycloadducts have been characterized; i.e., a) the [2+4]- and [2+6]photocycloadducts, from conjugated olefins, were normally stable and not dealdolyzed under mild conditions[6,8] and b) as a [2+2]cycloadduct, the protoadduct from *p*-isopropenyltoluene with **1a** was obtained in a trace amount after silica-gel column chromatography.[9] The present case, the isolation of stable compounds having two aldol groups as parts of a strained cyclobutane ring, seems to be quite extraordinary.

Experimental

Photodimerization of 1a. A mixed solution of benzene (6.5 cm^3) and cyclohexane (4.5 cm^3) of **1a** (884 mg) was irradiated through a Pyrex-glass filter with a 400-W high-pressure mercury lamp cooled with an ice-water for 12 h. Crystalline solid separated out was collected by filtration, and recrystallized from benzene to give **2a** [colorless needles, mp 135—136 °C, 153.4 mg; 17%. Found: C, 50.05; H, 5.71%. Calcd for $C_{12}H_{16}O_8$: C, 50.00; H, 5.50%. ^{1}H NMR δ[10]=2.20 (6H, s), 3.89 (6H, s), 4.24 (2H, s), and 4.58 (2H, s). ^{13}C NMR δ=29.3 (2C), 48.6 (2C), 53.4 (2C), 79.3 (2C), 169.9 (2C), and 205.3 (2C). *m/z*, 288 (M$^+$, 0.7), 271 (4), 201 (8), 169 (12), 159 (14), 145 (23), 143 (9), 141 (23), 99 (33), 84 (37), and 43 (100)].

Photodimerization of 1b. Similarly, irradiation of **1b** (349 mg) gave **2b** [colorless crystals, mp 114—115 °C, 35 mg; 10%. Found: C, 52.78; H, 6.55%. Calcd for $C_{14}H_{20}O_8$: C, 53.16; H, 6.33%. ^{1}H NMR δ=1.34 (6H, t, J=7 Hz), 2.28 (6H, s), 4.22 (2H, s), 4.32 (4H, q, J=7 Hz), and 4.45 (2H, br s). ^{13}C NMR (acetone-d_6) δ=14.3 (2C), 49.4 (2C), 62.5 (2C), 81.3 (2C), 169.8 (2C), and 203.7 (2C)].

X-Ray Analysis of 2a. Crystal and intensity data were collected on an Enraf-Nonius CAD 4 Diffractometer using Graphite monochromated Mo $K\alpha$ radiation. Crystal data: $C_{12}H_{16}O_8$, M.W., 288.25; monoclinic, Space group, $C_{2/c}$; a=15.6873(9), b=6.4078(4), c=14.6453(8) 10^{-8} cm, β= 116.23(5)°. D_c=1.450 g cm^{-3} for Z=4. The intensities of 3195 reflections were measured and 603 independent reflections within a 2θ angle range of 2° through 54° were used for analysis. The structure was solved by MULTAN 78 and the positional and thermal parameters were refined by a full-matrix least-square method; anisotropic thermal parameters for all non-H atoms and fixed isotropic thermal parameters for H atoms (4.0×10^{-16} cm^2). The final R values were found to be 8.1%.[11]

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5) Regioselective formation of the photocycloadducts from the exclusive tautomeric form of **1a**, methyl 2-hydroxy-4-oxo-2-pentenoate, can be interpreted that even the γ-hydrogen abstraction process by the excited carbonyl of the chelated hydroxyl, a chemical reaction, acuses the deactivation. Under such circumstances, an anti-Franck–Condon geometrical change should not be involved in the dimerization.

6) Indeed, the proto-photocycloadducts isolated from cyclopentadiene and **1a** have been established to have this cis relationship. See H. Takeshita, A. Mori, and Y. Toyonaga, *Bull. Chem. Soc. Jpn.*, **48**, 307 (1975).

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10) The NMR spectra were measured with a GSX 270 H Spectrometer, JEOL, in $CDCl_3$ solution unless otherwise specified.

11) The complete F_o–F_c data are deposited as Document No. 8865 at the Office of the Editor of Bull. Chem. Soc. Jpn.