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Photochemical Reactions of 4-Oxo Carboxylic Esters: Remote Hydrogen Abstraction and Cis–Trans Isomerization

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Synopsis. Upon irradiation, 2-benzyloxyethyl and 2-methoxyethyl 2-benzoylbenzoate underwent photocyclization through remote θ-hydrogen abstraction, though 2-benzyloxyethyl 3-benzoylacrylate underwent only cis–trans photoisomerization and 2-benzyloxyethyl 3-benzoylpropionate gave an intractable mixture. Conformational restriction is an important factor for remote hydrogen abstraction.

Intramolecular hydrogen abstraction by an excited carbonyl group through a six-membered cyclic transition state is a familiar photochemical process in carbonyl compounds and is known as the Norrish Type II reaction.[1)] However, hydrogen atom abstraction through a medium-sized cyclic transition state is a very rare event in the photochemistry of carbonyl compounds[2–5)] because of stereoelectronic requirements.[6)] We have reported that ω-(dialkylamino)alkyl benzoylacetates[7)] and benzoylpropionates[8)] underwent photocyclization through a remote proton transfer from their charge-transfer state to give medium-sized azalactones, and that ω-phenylalkyl and ω-(benzyloxy)alkyl benzoylacetates underwent photocyclization through direct remote hydrogen atom abstraction from their n,π* triplet states.[9)] The conformational flexibility and stability of the formed radical centers were found to be important factors for these photoreactions through medium-sized cyclic transition states. We report here on the photoreaction of 4-oxo carboxylic esters in order to provide evidence concerning the importance of a conformational restriction in remote hydrogen abstraction.

Remote hydrogen abstraction in a 3-oxo carboxylic esters can be achieved through more than a nine-membered cyclic transition state.[7,9)] Then, 2-benzyloxyethyl 3-benzoylpropionate (**1**) is expected to undergo hydrogen abstraction through an eleven-membered cyclic transition state. However, the irradiation of **1** in benzene under nitrogen with a 450 W high-pressure mercury lamp through a Pyrex filter gave an intractable mixture. The difference in the photochemical behavior of **1** from that of 3-benzyloxypropyl benzoylacetate,[9)] which undergoes photocyclization through the same sized-cyclic transition state as that expected in **1**, might indicate that the bond angles which are altered by a permutation of elements are quite important factors concerning the statistical probability of the approach of θ-hydrogen to an excited carbonyl oxygen.

A decrease in the conformational flexibility must increase the statistical probability of the approach of a θ-hydrogen atom to the excited carbonyl oxygen, and to cause remote hydrogen abstraction. In the *Z*-form of 2-benzoylacrylate (*Z*)-**2**, which is expected to be produced by irradiation of its *E*-isomer, the probability should be much higher than that for **1**. When (*E*)-**2** was irradiated under the same conditions as those for **1**, although isomerization to (*Z*)-**2** was observed, no products arising from remote hydrogen abstraction could be detected. Similarly, the irradiation of (*Z*)-**2** gave only (*E*)-**2**. The photoisomerization proceeded quantitatively from both isomers and the ratio of (*E*)-**2**/(*Z*)-**2** at the photostationary state was 4/96. (Fig. 1) We have suggested that the rate-determining process in remote hydrogen abstraction is not in the hydrogen abstraction process, but in the conformational change to a suitable conformer for hydrogen abstraction, and pointed out that the conformational flexibility is the important factor concerning abstraction.[7)] The fact that remote hydrogen abstraction cannot compete with photoisomerization in **2** indicates the presence of another limiting factor for abstraction. That is, the presence of the double bond in the linear chain in the molecule prevents remote hydrogen abstraction because of the faster deactivation causing the cis–trans isomerization.

Rigid cisoidal fixing of the molecular chain, such as ortho-fixing, might cause remote hydrogen abstraction. When 2-benzyloxyethyl 2-benzoylbenzoate (**3a**) was irradiated, the expected medium-sized hydroxylactone **4a** was obtained in 21% yield, together with 8% of tetracyclic compound **5**. The formation of compound **5** can be explained in terms of lactonization of the pinacol from **3a**. Stabilization of the radical center by

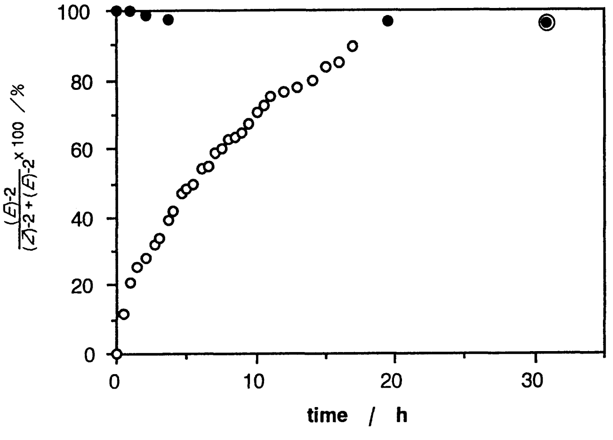
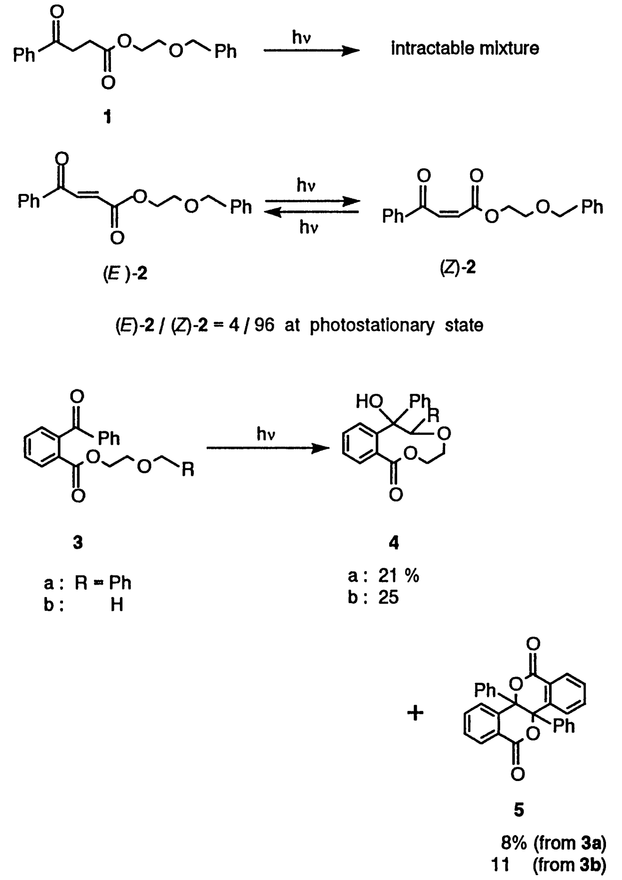


Fig. 1. Photoisomerization of (*E*)-**2** (○) and (*Z*)-**2** (●).

the phenyl group in a biradical intermediate is required for remote hydrogen abstraction in the 3-oxo carboxylic esters.[9] However, such an activation of an abstractable hydrogen atom was not required in the 4-oxo carboxylic esters. Irradiation of 2-methoxyethyl 2-benzoylbenzoate (**3b**) also gave lactone **4b** and **5** in 25 and 11% yields, respectively. The photocyclization of **3** provides evidence that conformational restriction is an important factor concerning the remote hydrogen abstraction. A decrease in the rotational freedom around the C_α–C_β bond increase the population of suitable conformers for remote hydrogen abstraction. The photoreaction of **3a** was efficiently quenched with 2,5-dimethyl-2,4-hexadiene, indicating that photoreaction occurred from the n,π* triplet excited state.



Scheme 1.

In conclusion, ortho fixing of the C_α–C_β bond of 4-oxo carboxylic esters decreases the conformational flexibility and increases the population of suitable conformers for remote hydrogen abstraction. On the other hand, fixing by a C=C double bond results in cis-trans photoisomerization as the sole photochemical process.

Experimental

The IR spectra were recorded with a JASCO IR Report-100 spectroneter; the ^{1}H and ^{13}C NMR spectra were measured with a JEOL FX90Q spectrometer using tetramethylsilane as an internal standard. An Ushio 450-W high-pressure mercury lamp was used as an irradiation source. The 4-oxo carboxylic esters, **1**—**3**, were prepared, by esterification of the corresponding acids.

General Procedure for Irradiation of 2 and 3. A solution of the 4-oxo carboxylic ester, **2** or **3** (ca. 2 mmol), in 50 cm^3 of benzene was irradiated under nitrogen with a 450-W high-pressure mercury lamp through a Pyrex filter. After removing the solvent the residue was chromatographed on a silica-gel column. Elution with a mixture of benzene and ethyl acetate gave the isomer of **2**, or **4** and **5**.

2-Benzyloxyethyl (*E*)-3-Benzoylacrylate ((*E*)-2): Bp 138 °C/3 mmHg (1 mmHg=133.322 Pa); IR (neat) 1740 and 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.74 (2H, t, J=4.6 Hz, CH_2O), 4.39 (2H, t, J=4.6 Hz, CO_2CH_2), 4.58 (2H, s, CH_2Ph), 6.89 (1H, d, J=15.7 Hz, olefinic), 7.2—7.6 (9H, m, aromatic+olefinic), and 7.8—8.0 (2H, m, aromatic). Found: C, 73.27; H, 5.85%. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85%.

2-Benzyloxyethyl (*Z*)-3-Benzoylacrylate ((*Z*)-2) was colorless liquid and isomerized to the *E*-isomer by heating. IR (neat) 1735 and 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.50 (2H, t, J=4.6 Hz, CH_2O), 4.17 (2H, t, J=4.6 Hz, CO_2CH_2), 4.43 (2H, s, CH_2Ph), 6.29 (1H, d, J=12.1 Hz, olefinic), 6.89 (1H, d, J=12.1 Hz, olefinic), 7.1—7.6 (8H, m, aromatic), and 7.8—8.0 (2H, m, aromatic).

1,2-Benzo-9-hydroxy-8,9-diphenyl-4,7-dioxa-1-cyclononen-3-one (4a): Mp 173.5—175.0 °C; IR (KBr) 3400 and 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.67 (1H, bs, OH), 3.2—3.7 (4H, m, CH_2), 5.03 (1H, s, CHPh), and 6.9—7.9 (14H, m, aromatic). Found: C, 76.66; H, 5.77%. Calcd for $C_{23}H_{24}O_4$: C, 76.66; H, 5.59%.

1,2-Benzo-9-hydroxy-9-phenyl-4,7-dioxa-1-cyclononen-3-one (4b): Colorless viscous oil; IR (neat) 3500 and 1780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.23 (1H, bs, OH), 3.55 (4H, bs, CH_2), 4.16 (2H, s, CO_2CH_2), and 7.1—8.0 (9H, m, aromatic); ^{13}C NMR δ=61.1 (t), 73.1 (t), 75.0 (t), 88.8 (s), 122.8 (d), 124.8 (d, 2C), 126.3 (s), 128.5 (d, 2C), 129.2 (d, 2C), 133.9 (d, 2C), 137.1 (s), 149.9 (s), and 169.5 (s). Found: C, 71.52; H, 5.80%. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67%.

4b,10b-Dihydro-4b,10b-diphenyl-6*H*,12*H*-5,11-dioxachrysene-6,12-dione (5): Mp 285—290 °C; IR (KBr) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.0—8.4 (18H, m, aromatic). Found: C, 80.21; H, 4.59%. Calcd for $C_{28}H_{18}O_4$; C, 80.37; H, 4.34%.

Rate Determination of Photoisomerization of 2. The acrylate (*E*)-**2** or (*Z*)-**2** was dissolved in benzene-d_6 (ca. 0.3 mol dm^{-3}) and placed in an NMR tube. After the tube was degassed by three freeze-pump-thaw cycles, it was sealed and then irradiated with a 450 W high-pressure mercury lamp through an aqueous solution of K_2CrO_4 (0.27 g dm^{-3}) and Na_2CO_3 (1 g dm^{-3}) to isolate the 313 nm line.[10] The amount of isomer produced was determined by an NMR analysis of the irradiated mixture.

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