Photocyclization of β-Oxoesters: Limiting Factors for Remote Hydrogen Abstraction through a Medium-sized Cyclic Transition State

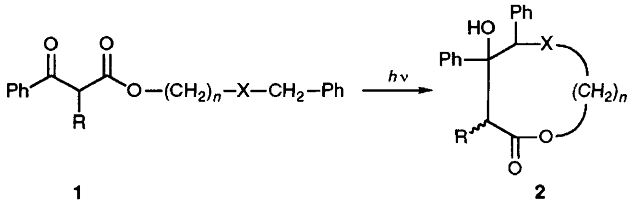
Tadashi Hasegawa,*[a] Yumiko Horikoshi,[a] Satoko Iwata[a] and Michikazu Yoshioka[b]

[a] Department of Chemistry, Tokyo Gakugei University, Nukuikitamachi, Koganei, Tokyo 184, Japan
[b] Department of Chemistry, Saitama University, Shimo-okubo, Urawa, Saitama 338, Japan

On irradiation, the ω-phenylalkyl β-oxoesters **1** undergo photocyclization *via* remote hydrogen abstraction through a cyclic transition state of at least nine atoms.

Intramolecular γ-hydrogen abstraction by the excited carbonyl, known as the Norrish Type II reaction, is one of the most well-known photochemical primary processes and generally takes place in preference to other possible modes.[1] The predominance is attributable to stereoelectronic[2] or geometric[3] favourableness in the γ-hydrogen abstraction. There are a few examples of hydrogen abstraction through medium-sized cyclic transition states,[4,5] but there are no systematic studies for the effects of the ring size for the transition states. We previously reported that (ω-dialkylamino)alkyl esters of β-[6] and δ-oxoacids[7] underwent photocyclization *via* remote hydrogen transfer through medium-sized cyclic transition states from the charge-transfer states. We report here on the photocyclization of β-oxoesters **1** through direct remote hydrogen abstraction by the excited ketone carbonyl group and the geometrical limitation of the cyclic-transition state for the abstraction.

Irradiation of a benzene solution of 2-benzyloxyethyl benzoylacetate **1a** under nitrogen with a 450 W high-pressure mercury lamp through a Pyrex filter gave the oxalactone **2a** in 48% yield. Only one isomer could be obtained from two possible stereoisomers with respect to the two phenyl groups. The configuration of **2a** is probably *trans* because of the less steric repulsion between the two phenyl groups. The IR



1 **2**

	R	X	*n*	Ring size of transition state	Yield of **2** (*cis*/*trans*) (%)
a:	H	O	2	10	48
b:	Me	O	2	10	76 (36/40)
c:	Me	CH_2	2	10	50 (20/30)
d:	Me	CH_2	1	9	63 (32/31)
e:	Me	CH_2	0	8	0
f:	Me	—	0	7	0

spectrum of **2a** showed the characteristic hydroxy (3550 cm^{-1}) and lactone carbonyl (1705 cm^{-1}) absorptions. Similarly, irradiation of the 2-methylbenzoylacetate **1b** gave a pair of isomers **2b**, which probably have two *trans* phenyl groups and *cis* and *trans* C-7-methyl group toward C-6-phenyl group. The formation of the lactones **2a** and **2b** can be reasonably explained in terms of photocyclization through direct abstraction of η-hydrogen by the excited ketone carbonyl group, *via* a ten-membered cyclic transition state. Although η-hydrogens in **1a** and **1b** are activated by ether oxygen, this type of activation is not required in the remote hydrogen abstraction. Irradiation of the 4-phenylbutyl ester **1c** which has no ether oxygen activating the η-hydrogen under the same conditions also gave the lactone **2c**.

The size of the cyclic transition state must be a determining factor for the remote hydrogen abstraction. Irradiation of **1d** gave a pair of the isomers of the seven-membered lactone **2d**. The formation of **2d** is rationalized by ζ-hydrogen abstraction occurring through a nine-membered cyclic transition state. On the other hand, irradiation of **1e**, expecting ε-hydrogen abstraction through an eight-membered transition state, gave no cyclization products. These results indicate that the limiting size of the cyclic transition state for the remote hydrogen abstraction in **1** is nine atoms. The conformational restraints might be important for the remote hydrogen abstraction. However, other factors may serve for the remote hydrogen abstraction since irradiation of butyl or pentyl benzoylacetate or benzyl 2-methylbenzoylacetate **1f** gave no lactones. The benzylic δ-hydrogens in **1f** might have reduced reactivities due to the carboxy group.[8] The present work indicates that neither the charge-transfer character nor activation of abstractable hydrogens by hetero atoms nor special geometrical fixing is necessary for the remote hydrogen abstraction in **1**, but stabilization of the alkyl radical centre by conjugation with a group such as phenyl is required.

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