γ- *versus* δ-Hydrogen Abstraction in the Photochemistry of α-Alkyl β-Oxoamides

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The excited ketone carbonyl group in the α-alkyl β-oxoamide (**1a**—**e**) abstracts γ- and δ-hydrogen competitively from the n,π* triplet state; the δ-hydrogen abstraction greatly predominates over the γ-hydrogen abstraction in the photolyses of (**1c**) and (**1d**).

Intramolecular hydrogen abstraction by oxygen atoms of carbonyl groups in excited states is a well known primary photochemical process of carbonyl compounds.[1] In general the most favourable intramolecular hydrogen abstraction involves a six-membered cyclic transition state in the hydrogen abstraction step because of the stereoelectronic requirement for the abstraction.[2] Hydrogen abstraction involving a seven-membered cyclic transition state takes place only when γ-hydrogens are absent or δ-hydrogens are activated by substituents.[3] We have previously reported that *N,N*-dialkyl β-oxoamides underwent photocyclization *via* δ-hydrogen abstraction to give pyrrolidin-2-ones in high yields.[4] We report here the competing γ- and δ-hydrogen abstraction by ketone carbonyl groups in photolyses of the α-alkyl β-oxoamides (**1a**—**d**), and provide the first example of δ-hydrogen abstraction predominating greatly over γ-hydrogen abstraction.

When a methanol solution of *N,N*-dibenzyl-2-benzoyl-4-methylvaleramide (**1a**) was irradiated under nitrogen with light from a 450 W high-pressure mercury lamp through a Pyrex filter, the benzoylacetamide (**2a**) and the pyrrolidinone (**3a**) were obtained in 86 and 11% yield (Table 1), respectively. Similarly, irradiation of the β-oxoamide (**1b**) under the same conditions gave the acetamide (**2a**) and the pyrrolidinone (**3b**) in 71 and 28% yield, respectively. The ratio of the benzoylacetamide to the pyrrolidinone was quite different in photolyses of the α-ethyl-β-oxoamides (**1c**) and (**1d**). Irradiation of the β-oxoamide (**1c**) under the same conditions gave the benzoylacetamide (**2a**) and the pyrrolidin-2-one (**3c**) in 20 and 72% yield, respectively. Similarly, irradiation of the *N,N*-diethyl-β-oxoamide (**1d**) gave the benzoylacetamide (**2b**) and the pyrrolidinone (**3d**) in 27 and 66% yield, respectively.

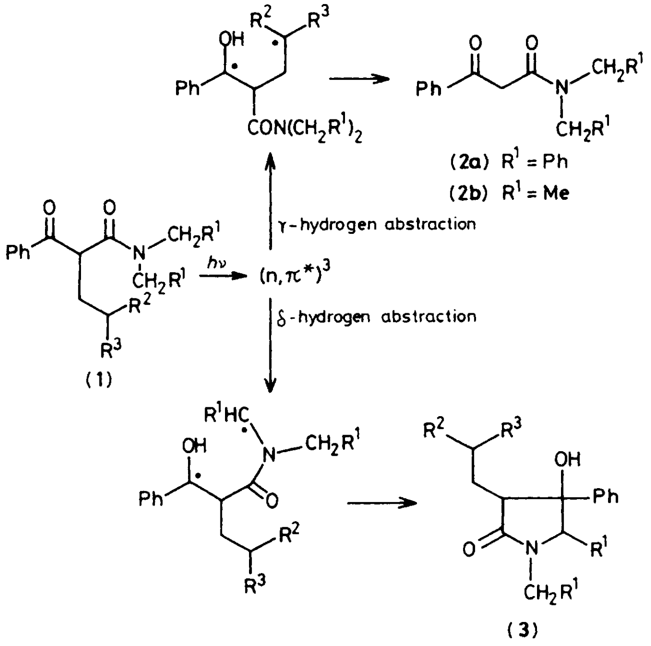

Table 1. Irradiation of the β-oxoamides (**1**).

Compound	R¹	R²	R³	% Yield (2a)	or (2b)	% Yield of (3)	δ:γ reactivity ratio
(**1a**)	Ph	Me	Me	86		11	0.13
(**1b**)	Ph	Me	H	71		28	0.39
(**1c**)	Ph	H	H	20		72	3.60
(**1d**)	Me	H	H		27	66	2.44

Formation of the benzoylacetamide (**2a**) and (**2b**) and the pyrrolidin-2-one (**3**) can be rationalized in terms of Norrish Type II elimination and photocyclization *via* δ-hydrogen abstraction, respectively. The δ-hydrogen abstraction competed comparably with the stereoelectronically favoured γ-hydrogen abstraction in the photolyses of (**1a**) and (**1b**), and predominated greatly over γ-hydrogen abstraction for (**1c**) and (**1d**). These results indicate that the amide nitrogen in the β-oxoamides effectively activates the δ-hydrogen atoms. Formation of both the benzoylacetamide and the pyrrolidinone from the β-oxoamide (**1c**) were efficiently quenched with penta-1,3-diene, indicating that the reactions proceed from the n,π^* triplet excited state of the β-oxoamide (**1**). Production of the pyrrolidinone (**3**) *via* δ-hydrogen abstraction may be considered to proceed from the charge-transfer state of the β-oxoamide (**1**).[4] However, it is quite improbable that the rate of bimolecular quenching with penta-1,3-diene greatly surpasses the rate of intramolecular charge-transfer quenching.

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