## $\gamma$ - versus $\delta$ -Hydrogen Abstraction in the Photochemistry of $\alpha$ -Alkyl $\beta$ -Oxoamides

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The excited ketone carbonyl group in the  $\alpha$ -alkyl  $\beta$ -oxoamide (1a—e) abstracts  $\gamma$ - and  $\delta$ -hydrogen competitively from the  $n,\pi^*$  triplet state; the  $\delta$ -hydrogen abstraction greatly predominates over the  $\gamma$ -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.<sup>1</sup> 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 sevenmembered cyclic transition state takes place only when  $\gamma$ hydrogens are absent or  $\delta$ -hydrogens are activated by substituents.3 We have previously reported that N,N-dialkyl  $\beta$ -oxoamides underwent photocyclization via  $\delta$ -hydrogen abstraction to give pyrrolidin-2-ones in high yields.4 We report here the competing  $\gamma$ - and  $\delta$ -hydrogen abstraction by ketone carbonyl groups in photolyses of the  $\alpha$ -alkyl  $\beta$ -oxoamides (1a—d), and provide the first example of  $\delta$ -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  $\beta$ -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  $\alpha$ -ethyl- $\beta$ -oxoamides (1c) and (1d). Irradiation of the  $\beta$ -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- $\beta$ -oxoamide (1d) gave the benzoylacetamide (2b) and the pyrrolidinone (3d) in 27 and 66% yield, respectively.

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  $\delta$ -hydrogen abstraction, respectively. The  $\delta$ -hydrogen abstraction competed comparably with the stereoelectronically favoured  $\gamma$ -hydrogen abstraction in the photolyses of (1a) and (1b), and predominated greatly over  $\gamma$ -hydrogen abstraction for (1c) and (1d). These results indicate that the amide nitrogen in the

Ph 
$$\stackrel{R^2}{\longrightarrow}$$
  $\stackrel{R^3}{\longrightarrow}$   $\stackrel{O}{\longrightarrow}$   $\stackrel{O}{\longrightarrow}$   $\stackrel{CH_2R^1}{\longrightarrow}$   $\stackrel{CH_2R^1}{\longrightarrow}$ 

**Table 1.** Irradiation of the  $\beta$ -oxoamides (1).

Compound R <sup>1</sup> R <sup>2</sup> R	% Yield 3 (2a) or (2b)	% Yield of (3)	δ: γ reactivity ratio
(1a) Ph Me M	e 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

 $\beta$ -oxoamides effectively activates the  $\delta$ -hydrogen atoms. Formation of both the benzoylacetamide and the pyrrolidinone from the  $\beta$ -oxoamide (1c) were efficiently quenched with penta-1,3-diene, indicating that the reactions proceed from the

 $n,\pi^*$  triplet excited state of the  $\beta$ -oxoamide (1). Production of the pyrrolidinone (3) via  $\delta$ -hydrogen abstraction may be considered to proceed from the charge-transfer state of the  $\beta$ -oxoamide (1). 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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