

## Intramolecular Hydrogen Abstraction in Ketone Photochemistry: the First Examples of $\zeta$ -Hydrogen Abstraction

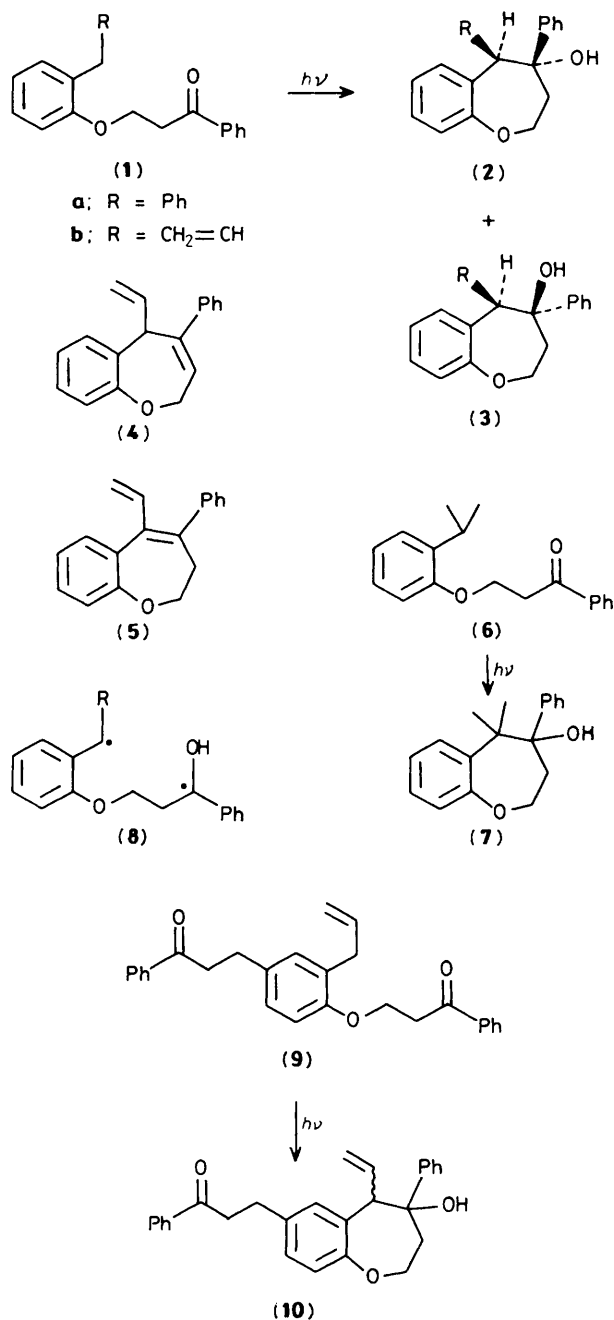
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U.v. irradiation of the aryl ketones (1), (6), and (9) leads to intramolecular hydrogen abstraction *via* a nine-membered transition state, yielding tetrahydrobenzoxepinols.

Intramolecular hydrogen abstraction by an excited carbonyl group is one of the best known of photochemical processes. Normally, it is  $\gamma$ -hydrogen atoms which are abstracted most rapidly, *via* a six-membered transition state, as in the Norrish type II reaction.<sup>1,2</sup> However, carbonyl compounds which lack suitably aligned  $\gamma$ -hydrogens by reason of conformation or substitution can still undergo efficient and high-yielding intramolecular abstraction which may involve  $\delta$ -hydrogen<sup>3</sup> or

$\epsilon$ -hydrogen<sup>4</sup> atoms. Abstraction from more remote positions has only rarely been observed, being associated with electron-transfer character, as in the photochemistry of imides<sup>5</sup> or amino-ketones.<sup>6</sup> Breslow<sup>7</sup> has provided elegant examples of biomimetic hydrogen abstraction, activated by aromatic carbonyl photoexcitation, occurring from remote sites. We now describe the first examples of  $\zeta$ -hydrogen abstraction in the photochemistry of simple carbonyl compounds, whereby



cyclisation of the resulting 1,7-biradicals leads to the formation of reduced benzoxepinols.

The *o*-benzyl substituted ketone (1a)<sup>†</sup> was a suitable candidate molecule in which to search for photochemical  $\zeta$ -hydrogen abstraction. U.v. irradiation of a solution of (1a) (0.23 g) in benzene (70 ml) was carried out for 50 h using Pyrex apparatus and a centrally-positioned 450 W medium-pressure mercury arc lamp. The two photoproducts (2a) and (3a) were separated by silica gel chromatography, in yields of 16 and 36%, respectively, and assigned the tetrahydrobenzoxepinol

<sup>†</sup> Ketones (1) and (6) were prepared from the stirred reaction at 20 °C of the appropriate 2-substituted phenol (1 equiv.) with acrylophenone (1 equiv., generated *in situ* from  $\beta$ -chloropropiophenone) in benzene in the presence of potassium carbonate (2 equiv.).

structures on the basis of spectroscopic evidence.<sup>‡</sup> Compound (2a) showed, *inter alia*,  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.03 and 2.71 (each ddd, H-3), 4.08 and 4.33 (each ddd, H-2), and 5.06 (s, H-5);  $\delta_{\text{C}}$  47.0 (C-3), 58.1 (C-5), 68.8 (C-2), and 75.1 (C-4), whereas compound (3a) showed  $\delta_{\text{H}}$  1.80 and 3.13 (H-3), 4.19 (d, *J* 1.2 Hz, H-5), and 4.40 (m, 2  $\times$  H-2);  $\delta_{\text{C}}$  38.3 (C-3), 67.1 (C-5), 67.6 (C-2), and 75.6 (C-4).

The allyl ketone (1b), irradiated under similar conditions (1 g in 200 ml of benzene solution), gave the two related stereoisomers (2b) and (3b) in a 2:1 ratio (33% isolated yield), along with polymeric material. After separation by chromatography, the stereochemistry of these cyclised tertiary alcohols was confirmed by the conversion of the major isomer (2b), using thionyl chloride and pyridine in benzene, exclusively into the dihydrobenzoxepine (4), whereas the minor isomer (3b) treated under these conditions gave a 1:2 mixture of (4) and (5), in agreement with the expectations of *anti*-elimination.

Irradiation of the *o*-isopropyl ketone (6) in benzene solution likewise gave cyclisation to yield the tetrahydrobenzoxepinol (7), isolated in 33% yield.

These examples of long-range photochemistry<sup>2,7,8</sup> presumably occur *via* a most unusual nine-membered transition state for hydrogen abstraction by the triplet excited carbonyl group, followed by cyclisation of the resulting 1,7-biradical (8). In our experiments, the quantum efficiencies for these processes are obviously low in comparison with those for  $\gamma$ - or  $\zeta$ -hydrogen abstraction, and there is some competition from intermolecular hydrogen abstraction, which leads to polymer formation. Nevertheless, we have been able to carry out  $\zeta$ -hydrogen abstraction selectively in a molecule containing two carbonyl functional groups. Thus, irradiation of the diketone (9)<sup>§</sup> gave the two separable cyclised products (10), isolated in 21% yield, in which the *para*-substituted  $\beta$ -benzoyl ethyl grouping has been retained during the photochemical reaction.

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<sup>‡</sup> All new compounds were characterised by <sup>1</sup>H and <sup>13</sup>C n.m.r., i.r., and mass spectra or analytical data.

<sup>§</sup> Prepared by reaction of 2-allylphenol with  $\beta$ -chloropropiophenone (2 equiv.) for 3 days at 20 °C, followed by a further 3 days stirring in benzene in the presence of potassium carbonate (2 equiv.).