Intramolecular Hydrogen Abstraction in Ketone Photochemistry: the First Examples of ζ-Hydrogen Abstraction

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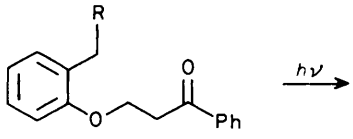
U.v. irradiation of the aryl ketones (**1**), (**6**), and (**9**) leads to intramolecular hydrogen abstraction *via* a nine-membered transition state, yielding tetrahydrobenzoxepinols.

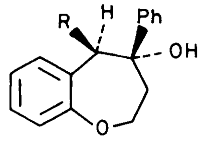
Intramolecular hydrogen abstraction by an excited carbonyl group is one of the best known of photochemical processes. Normally, it is γ-hydrogen atoms which are abstracted most rapidly, *via* a six-membered transition state, as in the Norrish type II reaction.[1,2] However, carbonyl compounds which lack suitably aligned γ-hydrogens by reason of conformation or substitution can still undergo efficient and high-yielding intramolecular abstraction which may involve δ-hydrogen[3] or ε-hydrogen[4] atoms. Abstraction from more remote positions has only rarely been observed, being associated with electron-transfer character, as in the photochemistry of imides[5] or amino-ketones.[6] Breslow[7] has provided elegant examples of biomimetic hydrogen abstraction, activated by aromatic carbonyl photoexcitation, occurring from remote sites. We now describe the first examples of ζ-hydrogen abstraction in the photochemistry of simple carbonyl compounds, whereby



(1)

a; R = Ph

b; R = $CH_2{=}CH$



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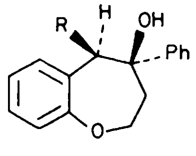

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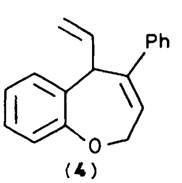

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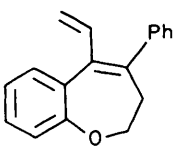

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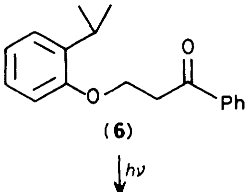
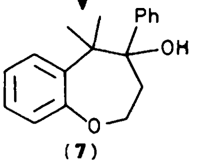
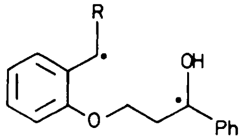


(6)



(7)



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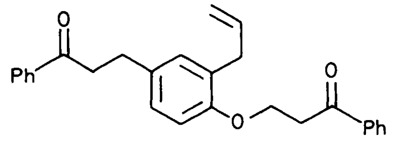
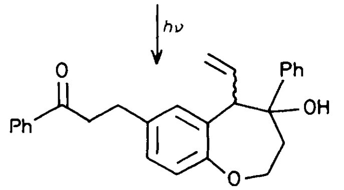


(9)



(10)

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

The *o*-benzyl substituted ketone (**1a**)† was a suitable candidate molecule in which to search for photochemical ζ-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 structures on the basis of spectroscopic evidence.‡ Compound (**2a**) showed, *inter alia*, δ_H ($CDCl_3$) 2.03 and 2.71 (each ddd, H-3), 4.08 and 4.33 (each ddd, H-2), and 5.06 (s, H-5); δ_C 47.0 (C-3), 58.1 (C-5), 68.8 (C-2), and 75.1 (C-4), whereas compound (**3a**) showed δ_H 1.80 and 3.13 (H-3), 4.19 (d, J 1.2 Hz, H-5), and 4.40 (m, 2 × H-2); δ_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[2,7,8] 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 γ- or ζ-hydrogen abstraction, and there is some competition from intermolecular hydrogen abstraction, which leads to polymer formation. Nevertheless, we have been able to carry out ζ-hydrogen abstraction selectively in a molecule containing two carbonyl functional groups. Thus, irradiation of the diketone (**9**)§ gave the two separable cyclised products (**10**), isolated in 21% yield, in which the *para*-substituted β-benzoylethyl grouping has been retained during the photochemical reaction.

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† 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 β-chloropropiophenone) in benzene in the presence of potassium carbonate (2 equiv.).

‡ All new compounds were characterised by ^1H and ^{13}C n.m.r., i.r., and mass spectra or analytical data.

§ Prepared by reaction of 2-allylphenol with β-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.).