δ- *versus* γ-Hydrogen Abstraction in the Photocyclization of β-Alkoxy-ketones

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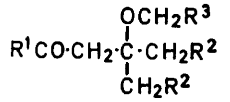
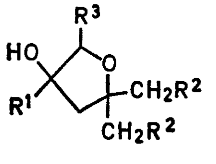
Summary Photocyclization of β-alkoxy-ketones can give tetrahydrofuranols and cyclobutanols *via* δ- or γ-hydrogen abstraction, respectively: the occurrence of δ-hydrogen abstraction *via* a seven-membered transition state is attributable to the enhanced stability of the resulting α-oxalkyl radical.

ULTRAVIOLET irradiation of the β-alkoxy-ketone (I) has been reported to give the tetrahydrofuranol (II) as a major product.[1,2] This product, which is considered to arise *via* δ-hydrogen abstraction by the oxygen atom of the excited carbonyl group to give the intermediate (III), was formed to the exclusion of the cyclobutanol (IV), the cyclization product that would arise by conventional γ-hydrogen abstraction[3] to give the intermediate (V).†



$R^1CO{\cdot}CH_2{\cdot}\overset{OCH_2R^3}{\underset{CH_2R^2}{C}}{\cdot}CH_2R^2$

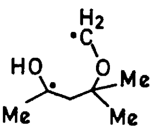
	R^1	R^2	R^3
(I)	Me	H	H
(VI)	Ph	H	H
(VII)	Ph	H	Me
(VIII)	Ph	Me	H
(IX)	Ph	Me	Me
(XVII)	Me	Me	H



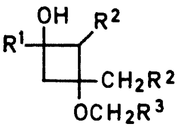
	R^1	R^2	R^3
(II)	Me	H	H
(X)	Ph	H	H
(XI)	Ph	H	Me
(XII)	Ph	Me	H
(XIII)	Ph	Me	Me
(XVIII)	Me	Me	H

Although departure from preferred γ-hydrogen abstraction has been observed in certain other cases,[4] these could be interpreted in terms of the greater propinquity to the carbonyl oxygen atom of other than γ-hydrogen. It appeared to us that a different factor favoured δ-hydrogen abstraction in the case of (I), the stabilization of the diradical (III) relative to (V), due to the presence of the ether oxygen atom. The facilitation of hydrogen abstraction by such stabilization is well documented.[5]

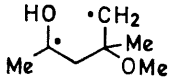
In order to test this hypothesis the photochemistry of the β-alkoxy-ketones (VI)—(IX) in pentane has been investigated. Several types of reaction pathway were observed in addition to cyclization, which included elimination of alcohol to give αβ-unsaturated ketones,[1] intermolecular reduction, and Norrish type I and II cleavages. However, as far as the cyclization reactions are concerned, a clear-cut dichotomy was observed between compounds (VI) and (VII), on the one hand, which gave rise to the tetrahydrofuranols (X) and (XI), respectively, but not to cyclobutanols, and compounds (VIII) and (IX), on the other, which gave rise to both tetrahydrofuranols [(XII) and (XIII), respectively] and to cyclobutanols [(XIV) and (XV), respectively].‡ This result is in good accord with the above hypothesis concerning the importance of the stability of the diradical formed by hydrogen abstraction, in that in the two cases where cyclization *via* γ-hydrogen abstraction is observed to occur in addition to cyclization *via* δ-hydrogen abstraction, additional stability is conferred on the corresponding diradical intermediate by virtue of the fact that it incorporates a secondary rather than a primary alkyl radical.§



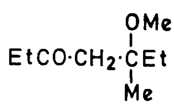
(III)



(IV) $R^1 = Me, R^2 = R^3 = H$
(XIV) $R^1 = Ph, R^2 = Me, R^3 = H$
(XV) $R^1 = Ph, R^2 = R^3 = Me$



(V)



$EtCO{\cdot}CH_2{\cdot}\overset{OMe}{\underset{Me}{C}}Et$

(XVI)

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† It may be noted that γ-hydrogen abstraction is favoured by a statistical factor of two.

‡ In some cases the formation of two diastereoisomeric forms of the tetrahydrofuranols and cyclobutanols was observed.

§ The fact that abstraction from the methylene group of a *C*-ethyl group is competitive with that from the methylene group of an *O*-ethyl group, while abstraction from a *C*-methyl group does not compete with that from an *O*-methyl group can be interpreted in terms of the conflicting effects produced by alkyl substitution at an α-oxalkyl radical centre *i.e.* hyperconjugative stabilization *versus* inductive destabilization.

Furthermore, it was found that Norrish type II cleavage, which also occurs *via* γ-hydrogen abstraction,[3] occurred in the case of (VIII) and (IX) but not of (VI) and (VII).

A similar observation was made in the case of the cyclization products from the ketone (XVI), which were of both the tetrahydrofuranol and cyclobutanol type, in contrast to the cases of (I) and (XVII), where only the tetrahydrofuranols (II) and (XVIII), respectively, were formed on cyclization.¶

Thus, the unusual occurrence of δ-hydrogen abstraction *via* a seven-membered transition state in the case of β-alkoxy-ketones can be attributed to the enhanced stability of the resulting α-oxalkyl radical.

We thank the National Research Council of Canada for support of this work.

(*Received, March 5th,* 1970; *Com.* 313.)

¶ Norrish type II cleavage has been reported as a minor photochemical pathway in the case of (I) (ref. 1). However, in the present work, such cleavage was not observed for (I) nor (XVII), but only for (XVI) (*cf.* also ref. 2a).

[1] D. J. Coyle, R. V. Peterson, and J. Heicklen, *J. Amer. Chem. Soc.*, **86**, 3850 (1964).

[2] The structural assignment was subsequently confirmed by other investigators; (a) A. G. Szabo, Ph.D. Thesis, Toronto, 1965; (b) M. A. Gianturco and P. Friedel, *Canad. J. Chem.*, 1965, **43**, 2121.

[3] *Cf., e.g.* P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, 1968, **5**, 21.

[4] *Cf., e.g.* N. C. Yang in "Proceedings of the 13th Conference on Chemistry, University of Brussels, 1965. Reactivity of the Photoexcited Organic Molecule," Interscience, New York, 1967, p. 145.

[5] *Cf., e.g.* A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, 1951, **19**, 329; F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, 1970, **92**, 311.