# Intramolecular Photoreactions of Enones

By B. D. Challand

(*Department of Science, Stockport College of Technology, Stockport,* SK1 3UQ,† *and Department of Chemistry, University of Western Ontario, London, Canada*)

*Summary* Three novel photochemical cyclisations of the enone and the acyl group in 2-acyloxy-enones are described.

The photochemistry of αβ-unsaturated ketones has been studied intensively in the past decade,[1] and typical reactions, such as cycloaddition with alkenes, have been

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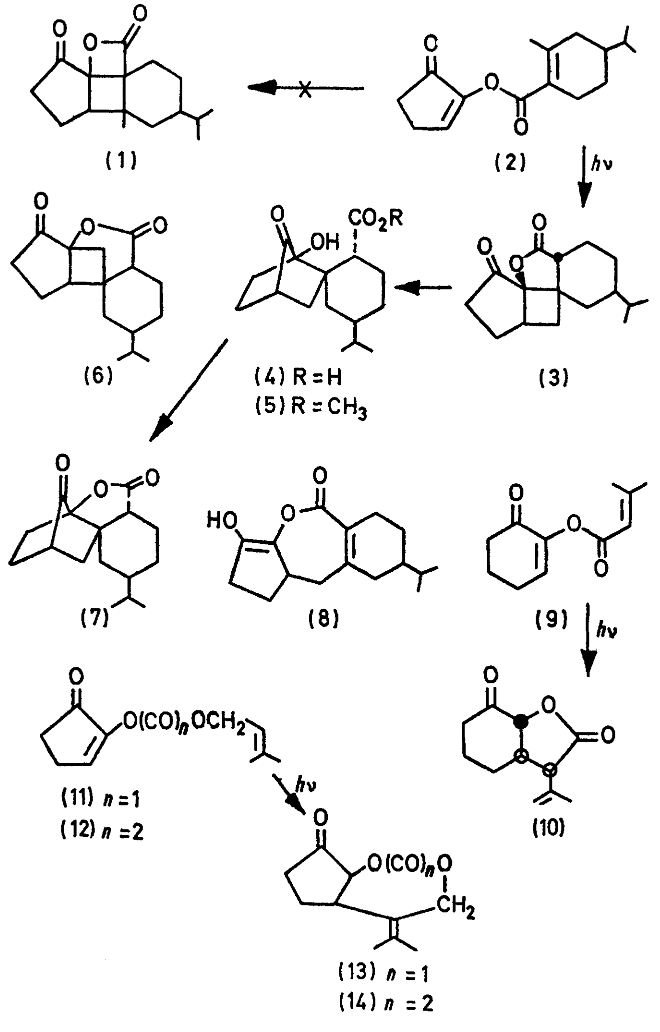
† Present address.

considerably used synthetically.[2] Intramolecular hydrogen abstraction, followed by addition of the resulting radicals, has also been reported on several occasions in cyclic and acyclic enone systems.[3,4] I report three novel types of photoreaction of cyclic enones.



During a study of cycloaddition reactions, an attempt was made to prepare the cyclobutane compound (1) by irradiation of the ester (2)‡ (cyclohexane solution, λ300—360 nm).[5] The major product (30% yield) proved not to be (1), but the isomer (3).‡ This structure was confirmed as follows. Alkaline hydrolysis and rearrangement to (4) was followed by methylation to give (5).‡ This rearrangement was expected, since it has been shown to be a general reaction of 1-hydroxybicyclo[3,2,0]heptan-2-ones.[6] The alternative formulation for the photoproduct, (6), was rejected after it was found that both (4) and (5) were converted by heating into the lactone (7) (showing i.r. absorption at 1790 and 1802 cm$^{-1}$). This observation also confirmed the stereochemistry shown for (3) and (5).

Formation of the photoproduct (3), rather than (1), was unexpected. It is possible (although unlikely with the wavelengths used) that an initial absorption of energy by the unsaturated ester caused deconjugation,[7] which was followed by a normal photocycloaddition. Alternatively an initial abstraction of an allylic hydrogen atom by the excited enone, *via* a nine-membered-ring transition state, might have been followed by cyclisation; this mechanism would require a final addition of the intermediate enol (8) to the unsaturated ester to account for the cyclobutane product. Hydrogen abstraction reactions by excited ketones *via* seven- and nine-membered-ring and larger transition states have been reported on several occasions,[4,8] and seem to be fairly common when the stereochemistry is favourable, or when the hydrogen atom involved is activated.

In order to investigate the generality of this type of photoaddition several compounds of similar structure were studied. Irradiation of the ester (9) (t-butyl alcohol solution, $\lambda > 290$ nm) gave one major product (30% yield), identified as (10).‡ Although no experiments were conducted specifically to ascertain the mechanism of this reaction, formation of this compound is consistent with initial abstraction of an allylic hydrogen atom (*via* a nine-membered-ring transition state), followed by addition of the delocalised allylic radical. Biradical intermediates in hydrogen abstraction reactions of this type would be expected to have lifetimes much longer than the 1,4-biradical intermediates in type II reactions of saturated ketones,[9] permitting several bond rotations before cyclisation.

Two other similar systems have been studied. Both (11)‡ and (12),‡ on irradiation ($\lambda > 300$ nm) in ether–cyclohexane, were converted in good yield (about 70%) into (13) and (14). These products, being unstable to chromatography, were not purified completely, but their structures were proved from their spectra and by degradation. Formation of these photoproducts is difficult to interpret in terms of an initial abstraction of hydrogen by the excited enone.

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‡ Compounds designated thus gave satisfactory elemental analyses. Spectra of all new compounds obtained were consistent with the structures assigned to them.

[1] P. de Mayo, *Accounts Chem. Res.*, 1971, **4**, 41; W. L. Dilling, *Chem. Rev.*, 1906, **66**, 673.
[2] P. G. Bauslaugh, *Synthesis*, 1970, **2**, 287; P. G. Sammes, *ibid.*, p. 636.
[3] A. B. Smith and W. C. Agosta, *Chem. Comm.*, 1971, 343; H. C. Chiang, M. C. Woods, Y. Nakadaira, and K. Nakanishi, *ibid.*, 1967, 1201.
[4] J. Meinwald and J. W. Kobzina, *J. Amer. Chem. Soc.*, 1969, **91**, 5177.
[5] B. D. Challand, Thesis, University of Western Ontario, 1968.
[6] D. Helmlinger, P. de Mayo, M. Nye, L. Westfelt, and R. B. Yeats, *Tetrahedron Letters*, 1970, 349.
[7] R. R. Rando and W. von E. Doering, *J. Org. Chem.*, 1968, **33**, 1671.
[8] R. Bishop and N. K. Hamer, *Chem. Comm.*, 1969, 804; R. Breslow and M. A. Winnick, *J. Amer. Chem. Soc.*, 1969, **91**, 3083; G. R. Lappin and J. S. Zannucci, *Chem. Comm.*, 1969, 1113.
[9] P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.