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The Photoaddition of 4-Hydroxycoumarin and *N*-Methyl-4-hydroxyquinol-2-one to Cyclohexene.[1]

by

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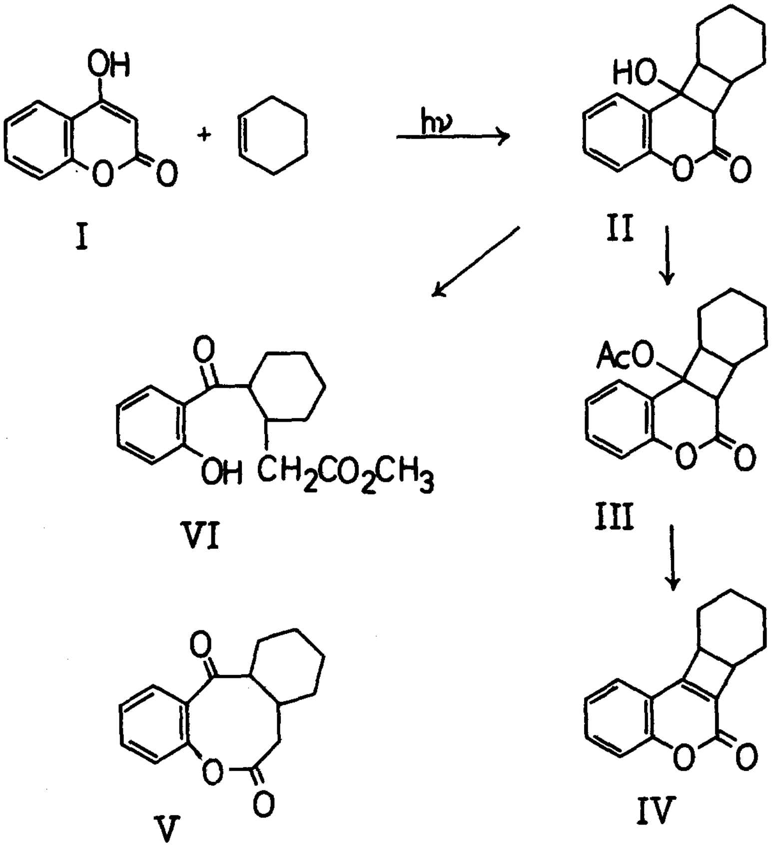
The photoaddition reaction of enolised β-dicarbonyl compounds to alkenes has been widely used in organic synthesis[2]; the cycloadducts thus formed readily undergo retro-aldol cleavage, a reaction sequence which in the case of cyclic β-diketones leads to ring expansion[3]. Previous studies have been principally concerned with aliphatic and alicyclic β-dicarbonyl compounds and their derived enol acetates. We now report the successful photoaddition of analogous heterocyclic systems, namely 4-hydroxycoumarin and *N*-methyl-4-hydroxyquinol-2-one, to cyclohexene, a reaction which has considerable potential as a synthetic route to 8-membered heterocycles.

A 0.062 M solution of 4-hydroxycoumarin (I) in cyclohexene-methanol (1:3) was irradiated through a silica filter with a medium pressure mercury arc until absorption at λ 327 nm, associated with 4-hydroxycoumarin, could no longer be detected. A crystalline adduct was isolated in 40% yield on removal of the solvent and had m.p. 117-118° (from ethanol), ν_{max} (CCl_4) 3590, 1755 and 1613 cm^{-1}, and δ ($CDCl_3$) 1.20 (8H, m), 2.84 (2H, m), 3.37 (1H, s), 3.50 (1H, d, J 8 Hz), and 7.30 (4H, m). The molecular formula was established as $C_{15}H_{16}O_3$ by analysis[4] and by mass spectra, m/e 244 (M^+). On the basis of this evidence, the adduct was assigned the cyclobutane structure (II). Coumarin itself is known to undergo analogous photosensitised cycloadditions to tetramethylethylene and cyclopentene[5].

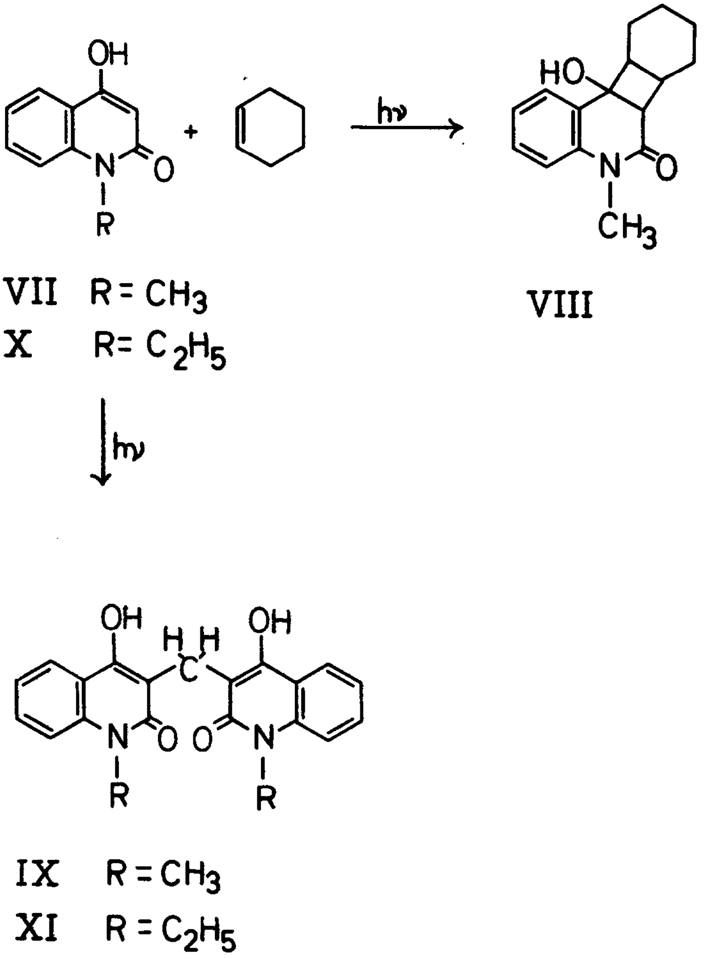
The adduct (II) was readily converted into the acetate (III), m.p. 195°, by treatment with boron trifluoride etherate in acetic acid. Pyrolysis of the acetate at 200° gave the cyclobutene (IV) and products derived therefrom. Full details of this elimination will be published elsewhere. Attempts to cleave the β-hydroxylactone function in the adduct (II) under a variety of conditions and obtain the oxepin (V) proved unsuccessful; in each case, reaction was accompanied by hydrolysis of the lactone. Thus, for example, the adduct (II) was converted into the ester (VI), b.p. 160-162°/0.4 mm Hg, ν_{max} 1740, 1638 and 1585 cm^{-1}, on treatment with piperidine in methanol. Although cleavage of the lactone clearly precludes the possibility of ring expansion in this case, analogous reactions in heterocyclic β-diketones which are not readily hydrolysed can be expected to be more successful.



An analogous adduct, m.p. 162°, ν_{max} (CH_2Cl_2) 3565, 1755 and 1620 cm^{-1}, was obtained from 4-hydroxycoumarin and cyclopentene; this was found to undergo a similar sequence of reactions. Irradiation of a 0.086 M solution of *N*-methyl-4-hydroxyquinol-2-one (VII) in cyclohexene-methanol (1:10) gave the corresponding adduct (VIII), m.p. 237-238°, ν_{max} (CCl_4) 3585, 1665 and 1600 cm^{-1}, m/e 257 (M^+), but in lower yield (14%). This can be partly attributed to the existence of competing reactions resulting from the use of increased amounts of methanol necessary to dissolve the quinolone. A separate study of the photochemistry of *N*-methyl-4-hydroxyquinol-2-one in methanol was therefore undertaken.

Irradiation of a 0.023 M solution of the quinolone (VII) in methanol gave an insoluble crystalline product in 35% yield with m.p. 285-295°, ν_{max} $(CHCl_3)$ 1640 and 1615 cm^{-1}, δ $(CDCl_3)$ 3.75 (6H, s), 4.0 (2H, s), 7.4 (8H, m) and 8.15 (2H, s), m/e 362 (M^+), 189 and 175. On the basis of this evidence, the photoproduct was assigned the structure (IX). This was confirmed by an unambiguous synthesis of the methylene bis-quinolone (IX) from *N*-methyl-4-hydroxyquinol-

2-one and formaldehyde, a reaction analogous to the condensation of dimedone with simple aldehydes. It is possible, therefore, that the only photochemical step implicated in the formation of photoproduct (IX) is one resulting in the formation of formaldehyde. In such an event, the precursor of formaldehyde remains unknown; irradiation of *N*-methyl-4-hydroxyquinol-2-one in ethanol affords the same adduct, virtually eliminating the solvent as a source of formaldehyde. The possibility that the *N*-methyl group of the quinolone could be the source of formaldehyde was also excluded by the observation that *N*-ethyl-4-hydroxyquinol-2-one (X) gave the corresponding methylene adduct (XI) m.p. 275° (from ethanol), m/e 390 (M^+), on irradiation in methanol.



VII R = CH_3

X R = C_2H_5

VIII

IX R = CH_3

XI R = C_2H_5

References

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3. See, for example, B. D. Challand, H. Hikino, G. Kornis, G. Lange, and P. de Mayo, *J.Org.Chem.*, 1969, *34*, 794.
4. Satisfactory analyses and spectra have been obtained for all new compounds.
5. J. W. Hanifin and E. Cohen, *Tetrahedron Letters*, 1966, 1419.