Synthesis of Cyclobuta[c]quinolin-3-ones. Intra- and Inter-molecular Photocycloadditions of 4-Alkoxy-2-quinolone Systems with Olefins

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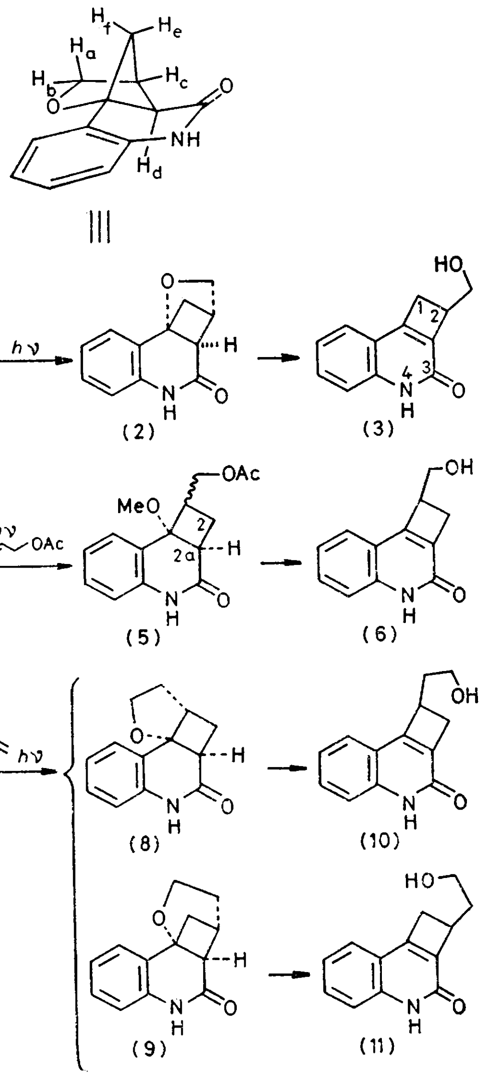
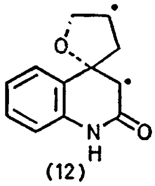
Summary Irradiation of 4-allyloxy-2-quinolone (**1**) gave the tetracyclic adduct (**2**) as the sole product, whereas 4-(but-3-enyloxy)-2-quinolone (**7**) led to a mixture (*ca.* 7 : 1) of adducts (**8**) and (**9**); base treatment of the adducts (**2**), (**8**), and (**9**) gave rise to the novel 1,2-dihydrocyclobuta[*c*]quinolin-3(4*H*)ones (**3**), (**10**), and (**11**) in quantitative yields.

THE intermolecular [2+2] photocycloadditions of 2-quinolone with olefins to give dihydrocyclobuta[*c*]quinolinones have been investigated extensively[1,2] and the nature of the product seems to be determined by 'the more stable biradical intermediate' theory and not by a dipole–dipole interaction mechanism.[1] These intermolecular cycloadditions have not been examined for 2-quinolones having a substituted 3,4-double bond,[3] and we now have found that the 3,4-double bond of 4-alkoxy-2-quinolones can add to olefins photochemically either intra- or inter-molecularly to give [2+2] adducts from which so far unknown 1,2-dihydrocyclobuta[*c*]quinolin-3(4*H*)-ones are obtained by base treatment.

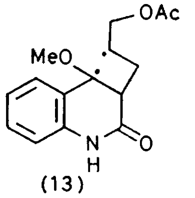


Irradiation of 4-allyloxy-2-quinolone[4] (**1**) in methanol resulted in the regio- and stereo-selective formation (85%) of the tetracyclic compound (**2**),† m.p. 178—179·5 °C. The stereostructure of (**2**) was assigned on the basis of its n.m.r. spectrum in which a large long-range coupling between the two *endo*-protons H$_d$ and H$_f$ was observed.[5] Treatment of (**2**) with sodium methoxide in methanol (reflux; 2 h) led to a quantitative yield of the 2-hydroxymethyl compound (**3**), m.p. 198—199 °C. The isomeric 1-hydroxymethyl derivative (**6**), m.p. 231—232 °C, was obtained in 60% overall yield by intermolecular photochemical cycloaddition of the 4-methoxy compound[4] (**4**) with allyl acetate (20 mol. equiv.) in dichloromethane followed by base treatment of the resulting head-to-tail adduct‡ (**5**), m.p. 174—175 °C.

In contrast to the regioselective addition observed with (**1**), irradiation of 4-(but-3-enyloxy)-2-quinolone (**7**), m.p. 186—186·5 °C, in methanol led to a mixture (80%) of the tetracyclic adducts (**8**), m.p. 195—195·5 °C, and (**9**), m.p. 193—194 °C (ratio *ca.* 7 : 1). These products both afforded the corresponding cyclobuta[*c*]quinolinones (**10**), m.p. 190—190·5 °C, and (**11**), m.p. 174·5—175 °C, in quantitative yields on base treatment.



(**12**)



(**13**)

We feel it reasonable to assume that the selective formation of the cross-addition product (**2**) occurs *via* the unstable biradical intermediate (**12**) which is probably formed under kinetic control, while (**5**) is formed *via* the stable biradical intermediate (**13**). The predominant formation of the parallel addition product (**8**) from (**7**) may be due to the presence of an extra methylene function in (**7**) compared with (**1**) which may facilitate the formation, by intermolecular cycloaddition, of a stable biradical intermediate similar to that in the formation of (**5**) owing to the steric flexibility of (**7**).

The present reactions open a new route to so far unknown cyclobuta[*c*]quinolinones and may be utilized in the synthesis of related ring systems.

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† All new compounds afforded satisfactory elemental analyses and spectroscopic data. Complete spectroscopic details, including ^{13}C n.m.r. spectra, will be given elsewhere.

‡ The [2+2] photo-cycloaddition of 2-quinolone and substituted olefins has been reported to give head-to-tail adducts regiospecifically (ref 1). The head-to-tail structure of (**5**) was confirmed by its n.m.r. spectrum in which 2a-H (δ 3·38) appeared as a triplet (J 10·0 Hz) indicating the presence of two protons on C-2.

[1] G. R. Evanega and D. L. Fabiny, *J. Org. Chem.*, 1970, **35**, 1757 and references cited therein.

[2] O. Buchardt, *Acta Chem. Scand.*, 1964, **18**, 1389.

[3] While 2-quinolones substituted in the benzene nucleus easily dimerized, 3- and 4-substitution seemed to hinder dimerization; see ref. 2 and M. Ishikawa, S. Yamada, H. Hotta, and C. Kaneko, *Chem. and Pharm. Bull.* (*Japan*), 1966, **14**, 1102.

[4] C. Kaneko, T. Naito, M. Hashiba, H. Fujii, and M. Somei, *Chem. and Pharm. Bull.* (*Japan*), 1979, **27**, 1813.

[5] Analysis of the n.m.r. spectrum (in $CDCl_3$) of (**2**) and related compounds [*e.g.*, the 2a-methyl derivative of (**2**)] allows the following assignments: H$_a$ and H$_b$, δ 4·14 (s), H$_c$, 3·51 (d), H$_d$, 2·79 (d), H$_e$, 2·66 (dd), and H$_f$, 1·68 (dd) with J_{ce} 2·9, J_{df} 9·5, and J_{ef} 8·3 Hz. Such large couplings are known to occur only if two protons in bicyclo[2.1.1]hexane or its hetero-analogues are in a W-configuration. A similar long-range coupling (7·8 Hz) was also observed in the corresponding protons of the adduct (**9**) (K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Amer. Chem. Soc.*, 1962, **84**, 1594; J. W. Gibson and W. F. Erman, *J. Org. Chem.*, 1972, **37**, 1148; Y. Tamura, H. Ishibashi, M. Hirai, Y. Kita, and M. Ikeda, *J. Org. Chem.*, 1975, **40**, 2702).