Tetrahedron Letters No. 28, pp 2637 - 2638.
© Pergamon Press Ltd. 1979. Printed in Great Britain.

0040-4039/79/0708-2637$02.00/0

INTRAMOLECULAR PHOTOCYCLOADDITION REACTIONS OF 4-ALKENYLOXYCOUMARINS [1]

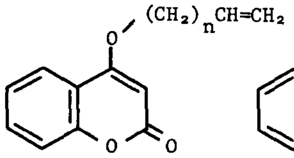
by David J. Haywood and Stewart T. Reid*,
University Chemical Laboratory,
Canterbury, Kent. CT2 7NH.

Intramolecular $[_{\pi}2 + _{\pi}2]$ photocycloaddition reactions are reported for 4-(but-3'-enyloxy) and 4-(pent-4'-enyloxy)coumarins.

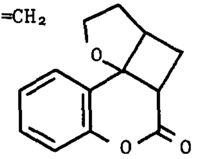
Intramolecular $[_{\pi}2 + _{\pi}2]$ photoaddition reactions have been widely reported. Analogous cycloadditions using enolised β-dicarbonyl compounds have also been described[2,3] and used, for example, in a synthesis of longifolene.[4] We have recently shown that intermolecular cycloaddition of heterocyclic enolised β-dicarbonyl compounds, namely 4-hydroxycoumarin[5] and 4-hydroxyquinol-2(1H)-one[6], to alkenes can be effected photochemically. We now report the intramolecular equivalent of this process using 4-alkenyloxycoumarins.

The 4-alkenyloxycoumarins (1a, b, c) were prepared by alkylation of 4-hydroxycoumarin with the appropriate bromoalkene in the presence of potassium carbonate.[7] Pyrex-filtered irradiation (medium pressure mercury arc) of 4-(but-3'-enyloxy)coumarin (1b) in benzene gave on distillation of the solvent and purification by tlc the intramolecular adduct (2), m.p. 85-86°, in 63% yield. The structural assignment rests on analytical and spectral data; ν_{max} (CH_2Cl_2) 1760, 1610 and 1100 cm^{-1}; δ_H ($CDCl_3$) 1.87 (1H, m), 2.1-2.5 (2H, m), 2.90 (1H, m), 3.50 (1H, m), 4.20 (1H, m), 4.45 (1H, m) and 7.0-7.8 (4H, m). The alternative adduct (3) is clearly eliminated from consideration by a careful examination of the 220 MHz ^1H n.m.r. spectrum. The signal at 3.50 δ, attributed to the methine proton at C-3 of the coumarin ring, is split (J 11.6 and 7.2 Hz) through coupling with the two adjacent methylene protons; further weak coupling with the other methine proton (J 1.6 Hz) is also observed. The ^{13}C n.m.r. spectra is in full agreement with the proposed structure: δ_C 25.8, 32.2, 40.8, 46.2, 68.9, 81.8, 117.1, 122.3, 125.1, 126.4, 130.1, 150.6 and 168.3

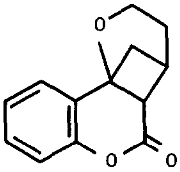
The intramolecular adduct (4), m.p. 110-111°, was similarly formed on irradiation in



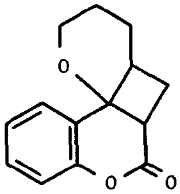
(1)a n = 1
b n = 2
c n = 3



(2)



(3)



(4)

benzene of 4-(pent-4'-enyloxy)coumarin (1c). The structure was established on the basis of spectral data and by analogy with the product of irradiation of 4-(but-3'-enyloxy)coumarin. Intramolecular addition was not observed, however, with 4-allyloxycoumarin (1a); prolonged irradiation in benzene gave rise to a dimer, m.p. 172-173°, to which the head-to-tail cyclobutane was assigned by comparison with the photodimer of 4-acetoxycoumarin.[8] The failure to undergo intramolecular cycloaddition in this case is perhaps surprising in view of the previously reported conversion of 3-allyloxy-5,5-dimethylcyclohex-2-en-1-one into a strained 2-oxabicyclo[2.1.1]hexane.

We thank the S.R.C. for a studentship (to D.J.H.) and Dr. C. Brown for assistance with the n.m.r. spectra.

References

1. Photochemical Transformations Part 12. For Part 11, see R.G.Hunt and S.T.Reid, J.C.S. Perkin I, 1977, 2462
2. Y.Tamura, H.Ishibashi, Y.Kita, and M.Ikeda, J.C.S.Chem.Comm., 1973, 101
3. M.Mellor, D.A.Otieno and G.Pattenden, J.C.S.Chem.Comm., 1978, 138
4. W.Oppolzer and T.Godel, J.Amer.Chem.Soc., 1978, **100**, 2583
5. D.J.Haywood, R.G.Hunt, C.J.Potter and S.T.Reid, J.C.S. Perkin I, 1977, 2458
6. R.G.Hunt, C.J.Potter, S.T.Reid and M.L.Roantree, Tetrahedron Letters, 1975, 2327
7. Satisfactory analyses and spectra have been obtained for all new compounds
8. Details to be published in a forthcoming paper
9. Y.Tamura, H.Ishibashi, M.Hirai, Y.Kita and K.Ikeda, J.Org.Chem., 1975, **40**, 2702

(Received in UK 18 April 1979)