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THE PHOTOISOMERISATION OF SOME BENZO[c]QUINOLIZINES.
THE ISOLATION OF THE FIRST 2H-QUINOLIZINE DERIVATIVE

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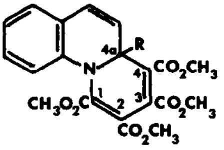
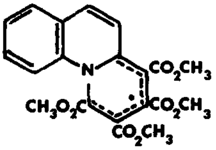
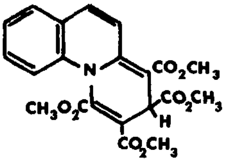
A large number of 9aH- and 4H- quinolizine derivatives have been reported[1], but no corresponding 2H-quinolizines have been isolated, although theoretical calculations[2] predict the order of stability as 4H > 2H > 9aH. I now wish to report the formation of the first 2H-quinolizine derivative (III).



Ia R = H
Ib R = D
Ic R = H, 1H tautomer



II



III

Irradiation of tetramethyl 4aH-benzo[c]quinolizine 1,2,3,4-tetracarboxylate (Ia) in dilute benzene solution in the presence of α-bromonaphthalene using a medium pressure mercury lamp gave a mixture of the isomeric 1H-benzo[c]quinolizine (Ic), a benzo[e]indolizine, a red dimer and an unstable product thought to be the 3H-benzo[c]quinolizine (III)†. Chromatography on neutral alumina gave (III) (pale yellow micro crystals, m.p. 146°, mass. spec. 413 (4%), 412 (20%), 354 (100%), 296, 237 (24%), 178 (60%), 128; u.v. 262 (11,100), 280* (10,900), 296 (11,200), 314 (10,100) and 400 (3,400); n.m.r. 7.3δ (4H), 8.32 (1H, d, J = 10.2 Hz.), 7.16 (1H,d, J = 10.2 hz.), 5.14 (1H, s), 3.85 (6H), 3.77 (3H) and 3.62 (3H)). Later fractions yielded the 1H-benzo[c]quinolizine (Ic) and a red dimer. The ultraviolet spectrum of the latter suggests it is a 1H-benzo[c]quinolizine (i.e. linkage at C_1). These results are in complete contrast to those obtained in methanol[3] when (Ia) was cleanly converted to (Ic).

† (III) is a derivative of 2H quinolizine - see numbering system in the diagram.

* = inflection

Structure (III) is based on the spectral data and the ready conversion to the 1H-benzo[c]quinolizine (Ic) in the presence of base. In the n.m.r. spectrum of (III) the angular 3H proton occurs as a singlet at 5.14δ and 5H as a doublet at 8.32δ, indicating strong deshielding by the C_4 ester group, as in (Ic). The mass spectrum of (III), shows the expected benzo[c]quinolizinium ions at m/e M-1 and M-59 (base peak).

Some (III) was also obtained on irradiation of (Ic) and it appears[4] that these isomerisations must involve the radical (II); a similar intermediate has been suggested for the dimerisation of some benzo[a]quinolizines[5]. An alternative mechanism involving a 1,3 sigmatropic shift is excluded as no deuterium is incorporated in (III) from the 4a-deuteroquinolizine (Ib).

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* The mechanistic detail will be discussed in the full paper.