The Photolysis of Some Benzo[*a*]quinolizines

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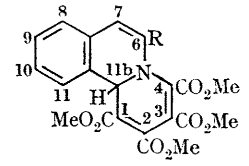
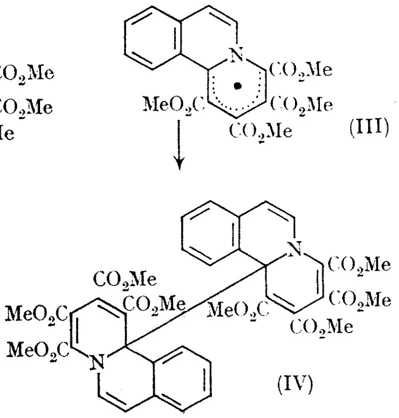
Summary Irradiation of both tetramethyl 11b*H*-benzo[*a*]quinolizine-1,2,3,4-tetracarboxylate and its 4*H*-isomer yield the same dimer as the major photochemical product.

THE photochemical products of the 11b*H*- and 4*H*-benzo[*a*]quinolizines[1] [(Ia) and (IIa), the "labile" and "stable" adducts of isoquinoline] have been examined. Irradiation of dilute benzene solutions of (Ia) and IIa) with a medium pressure mercury lamp, using 1-bromonaphthalene as photosensitiser gave the same yellow dimer, m.p. 282—283°; $C_{42}H_{36}N_2O_{16}$; mass spectrum, *m/e* 824, 765 (*M* — 59 base peak), 412 (second largest peak); u.v. 450 (ϵ 1080), 270 (2940), and 230 (2250) nm.; n.m.r. τ 2·6—2·9 (8H, m), 4·8 (2H, d, *J* 6·5 Hz.), 5·64 (2H, d, *J* 6·5 Hz.), 6·25 (12H), 6·40 (6H), and 6·55 (6H); i.r. ($CHCl_3$) (1400—1800 cm.$^{-1}$ region) 1738, 1790, 1620, and 1584, for which structure (IV) is suggested.

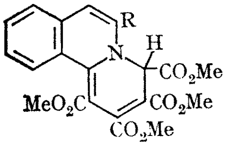


(Ia) R=H
(Ib) R=Me

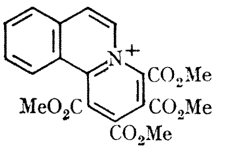


(III)

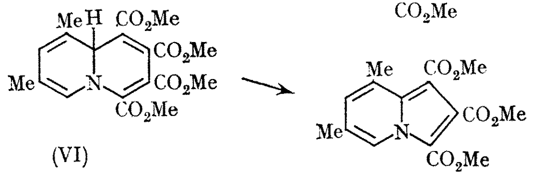
(IV)



(IIa) R=H
(IIb) R=Me



(V)



(VI)

(VII)

(IV) could arise by dimerisation of the radical (III), itself formed by loss of the 11b- and 4-hydrogens from (Ia) and (IIa), respectively. Linkage of the two quinolizine residues *via* the 11b-positions is preferred to alternatives since the u.v. spectrum of (IV) resembles that of (Ia), indicating that it possesses the "labile" adduct chromophore. The general pattern of the i.r. spectrum in the 1400—1800 region fits in well with the criteria laid down by Acheson and Hole[1] for the "labile" adducts. The most significant features of the n.m.r. spectrum are the two doublets for 6-H and 7-H at τ 4·8 and 5·64, which occur at much higher field than the corresponding protons of (Ia). Drieding models of (IV) show these protons to be heavily shielded by a benzenoid ring.

The mass spectrum of (IV) shows a weak parent ion (*m/e* 824), and like (Ia) shows a base peak at *M* — 59 (loss of CO_2Me). The second most abundant ion in the spectrum occurs at *m/e* 412 and is due to the stable ion (V).

In contrast to the above results, the 6-methylbenzo[*a*]quinolizine[2] (Ib) on photolysis under the same conditions was smoothly converted into its 4*H*-isomer (IIb). Photolysis of the 9a*H*-dimethylquinolizine[3] (VI) under similar conditions to those above resulted in ring contraction to the indolizine (VII).[3,4] When the photolyses of (Ia), (Ib), (IIa), and (VI) were carried out in the absence of 1-bromonaphthalene the starting materials were recovered unchanged in each case.

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[4] R. H. Wiley and L. H. Knabeschuh, *J. Org. Chem.*, 1953, **18**, 836.