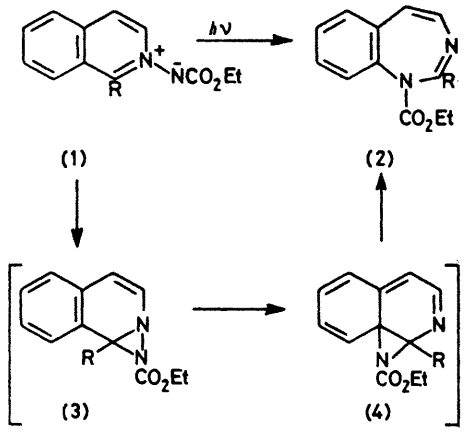
Formation of Novel 1*H*-1,3-Benzodiazepines in the Photolysis of Isoquinoline *N*-Imides

By TAKASHI TSUCHIYA,* MICHIKO ENKAKU, JYOJI KURITA, and HIROYUKI SAWANISHI
(*School of Pharmacy, Hokuriku University, Kanagawa-machi, Kanazawa* 920–11, *Japan*)

Summary Photolysis of the 1-substituted isoquinoline *N*-ethoxycarbonylimides (**1**) affords 1*H*-1,3-benzodiazepines (**2**) and the results of some reactions of this new ring are also reported.

IN connection with the photochemistry of various types of aza-aromatic *N*-imides such as pyridine,[1,2] quinoline,[3] pyrazine,[4] and benzocinnoline[5] *N*-imides, we were interested in examining the photochemical behaviour of isoquinoline *N*-imides. We now report that the photolysis of the *N*-

iminoisoquinoline imides (**1**) affords the previously unknown 1*H*-1,3-benzodiazepines (**2**) and some results of their reactions.



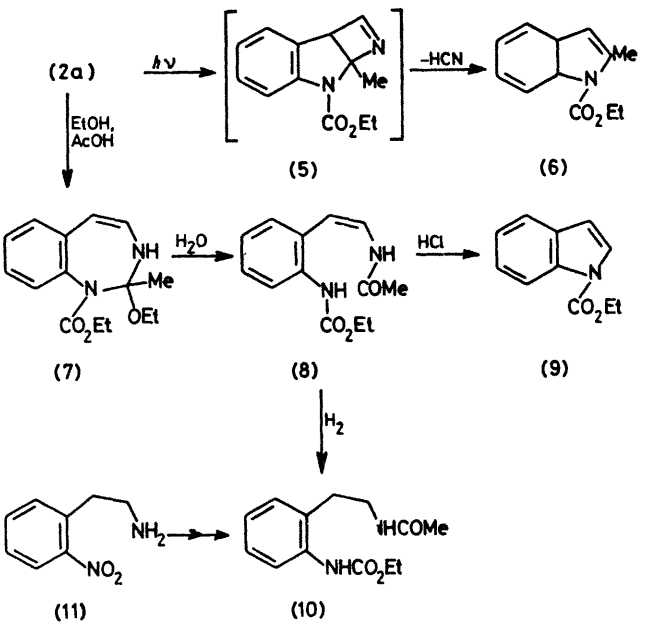
a; R = Me
b; R = CO_2Et

Irradiation (400 W, high-pressure Hg lamp; Pyrex filter) of the 1-substituted isoquinoline *N*-imides (**1**) for *ca.* 2 h in methylene chloride and chromatography over silica gel gave the 1*H*-1,3-benzodiazepines (**2**)† in *ca.* 20% yield. However, similar irradiation of 1-unsubstituted isoquinoline *N*-imides gave only 1-ethoxycarbonylaminoisoquinolines and no diazepines.

The formation of the diazepines (**2**) may involve ring expansion of the aziridine intermediates (**4**), which are formed *via* the diaziridines (**3**) by a [1,5] sigmatropic shift. Many examples[6] of this type of reaction involving a two-step rearrangement and ring-expansion have been reported in the photolysis of aromatic amine *N*-oxides, *e.g.*, isoquinoline[7] and quinazoline[8] *N*-oxides, which give the corresponding oxazepines and oxadiazepines. However, the present result is the first example for aromatic amine *N*-imides.

The spectral data of the new diazepines and the results of the following chemical studies are consistent with the proposed structures and eliminate other possible structures such as 2*H*- and 3*H*-2,3-benzodiazepines.

Further irradiation of the diazepine (**2a**) isolated resulted in the formation of the 2-methylindole (**6**) and HCN. The indole (**6**) may be formed *via* the tricyclic valence isomer (**5**) by analogy with triazepines[9] and 1,3-oxazepines,[7,8] but attempts to isolate the intermediate (**5**) failed.



Treatment of the diazepine (**2a**) with ethanol in the presence of acetic acid gave the adduct (**7**),‡ which was treated with water to give the ring-opened product (**8**). Compound (**8**) was treated with HCl to give 1-ethoxycarbonylindole (**9**) and was hydrogenated with Pd–C to give the dihydro compound (**10**), which was identical with an authentic sample prepared from *o*-nitrophenethylamine (**11**) by successive acetylation, reduction, and ethoxycarbonylation. These results are analogous to those observed for 1,3-benzoxazepines[7,8] and, thus, strongly support the structure of the new diazepine ring.

This work was supported by a Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture, Japan.

(*Received, 2nd April* 1979; *Com.* 335.)

† Satisfactory elemental analyses and spectral data were obtained for all new compounds reported, *e.g.*, (**2a**): m.p. 70—71·5 °C; λ (ε) (EtOH) 240 (9000) and 285 nm (5200); ν($CHCl_3$) 1710 cm^{-1}; δ ($CDCl_3$) 2·40 (3H, s, 2-Me), 6·44 (1H, d, *J* 9 Hz, 5–H), 6·92 (1H, d, 4–H), 7·1—7·5 (4H, m, Ar–H), and 1·26 and 4·18 (3H, t, and 2H, q, CO_2Et); (**2b**): m.p. 96·5—98 °C.

‡ Treatment of (**2a**) with MeOH in the presence of AcOH gave the methanol adduct. These adducts are unstable and readily converted into (**8**) during isolation.

[1] J. Streith, A. Blind, J.-M. Cassal, and C. Sigwalt, *Bull. Soc. chim. France*, 1969, 948; J. Streith, J. P. Luttringer, and M. Nastasi, *J. Org. Chem.*, 1971, **36**, 2962; T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *ibid.*, 1970, **35**, 426; A. Balasubramanian, J. M. McIntosh, and V. Snieckus, *ibid.*, p. 433.
[2] T. Tsuchiya, M. Enkaku, and H. Sawanishi, *Heterocycles*, 1978, **9**, 621.
[3] T. Tsuchiya, J. Kurita, H. Igeta, and V. Snieckus, *J.C.S. Chem. Comm.*, 1974, 640; T. Tsuchiya, J. Kurita, and V. Snieckus, *J. Org. Chem.*, 1977, **42**, 1856; and refs. cited therein.
[4] T. Tsuchiya, J. Kurita, and K. Ogawa, *J.C.S. Chem. Comm.*, 1976, 250.
[5] S. F. Gait, M. E. Peek, C. W. Rees, and R. C. Storr, *J.C.S. Perkin I*, 1975, 19.
[6] G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 1970, **70**, 231.
[7] C. Kaneko, S. Yamada, and M. Ishikawa, *Tetrahedron Letters*, 1966, 2145; O. Buchardt, C. Lohse, A. M. Duffield, and C. Djerassi, *ibid.*, 1967, 2741.
[8] C. Kaneko and S. Yamada, *Tetrahedron Letters*, 1967, 5233; G. F. Field and L. H. Sternbach, *J. Org. Chem.*, 1968, **33**, 4438; C. Lohse, *Tetrahedron Letters*, 1968, 5625.
[9] D. J. Anderson and A. Hassner, *J.C.S. Chem. Comm.*, 1974, 46; V. Nair, *J. Heterocyclic Chem.*, 1975, **12**, 183.