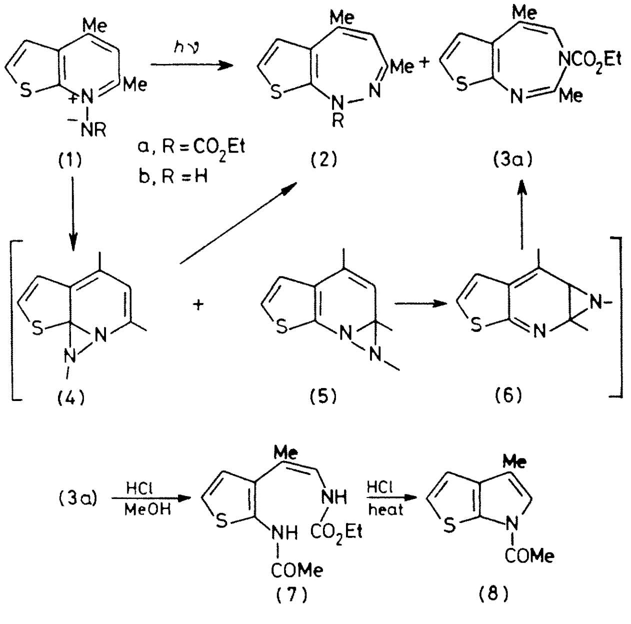
Photolysis of Thieno-, Furo-, and Pyrrolo-[*b*]pyridine *N*-Imides: Formation of 3*H*-1,3-Diazepines

By TAKASHI TSUCHIYA,* MICHIKO ENKAKU, and SATORU OKAJIMA
(*School of Pharmacy, Hokuriku University, Kanagawa-machi, Kanazawa,* 920–11, *Japan*)

Summary Photolysis of pyridine *N*-ethoxycarbonylimides condensed with thiophen, furan, and pyrrole rings on the *b*-side of the pyridine ring affords the corresponding novel 1*H*-1,2- and 3*H*-1,3-diazepines, respectively.

IT is known that 2-unsubstituted quinoline and related fused pyridine *N*-imides undergo photo-induced rearrangement to give the corresponding fused 1,2-diazepines and/or 2-aminopyridines.[1,2] We recently reported the formation of novel 1*H*-1,3-benzodiazepines in the photolysis of 1-substituted isoquinoline *N*-acylimides by a two-step rearrangement;[3] in contrast, irradiation of 1-unsubstituted isoquinoline *N*-imides gives only 1-aminoisoquinolines and no diazepines.[2,4] An analogous route to 3*H*-1,3-benzodiazepines from 2-substituted quinoline *N*-imides has not been successful to date. We now report that the photolysis of pyridine *N*-imides condensed with aromatic 5-membered heterocycles on the *b*-side of the pyridine ring affords the corresponding novel 3*H*-1,3-diazepines by a two-step rearrangement, the first example of this reaction for quinoline-type fused pyridine *N*-imides.

In a typical experiment (Scheme 1), irradiation (400 W high-pressure Hg lamp) of the thienopyridine *N*-imide (**1a**) for 2—3 h in benzene and chromatography over silica gel gave the 1*H*-1,2-diazepine (**2a**) and the 3*H*-1,3-diazepine (**3a**) in yields of 10—15 and 50—60%, respectively.†



SCHEME 1

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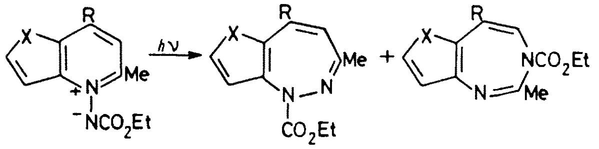
† Satisfactory elemental analyses and spectral data were obtained for all new compounds reported, *e.g.*, (**3a**): m.p. 67—68·5 °C; λ(ε) (EtOH) 228 (10,700) and 305 nm (2100); ν (KBr) 1700 cm^{-1}; δ ($CDCl_3$) 2·04 (3H, br, 5-Me), 2·40 (3H, s, 2-Me), 5·66 (1H, br, 4-H), 6·84 (1H, d, 6-H), 6·96 (1H, d, 7-H), and 1·28 and 4·14 (3H, t, and 2H, q, CO_2Et).

However, similar irradiation of the *N*-unsubstituted *N*-imide (**1b**) gave only the 1*H*-1,2-diazepine (**2b**) in *ca.* 60% yield and no 1,3-diazepine.

The formation of the diazepines may proceed by photoinduced rearrangement to two kinds of diaziridine intermediate, (**4**) and (**5**). The 1,2-diazepine (**2a**) is formed directly from (**4**), whereas the formation of the 1,3-diazepine (**3a**) involves ring-expansion of the aziridine intermediate (**6**) formed from (**5**) by a [1,5]-sigmatropic shift by analogy with 1*H*-1,3-benzodiazepines.[3] The initial rearrangement may take place to either side of the pyridine ring, in contrast with reactions of quinolines and isoquinolines.

The spectral data of the novel 1,3-diazepines and the following chemical results are consistent with the proposed structures. Treatment of (**3a**) with HCl in methanol at room temperature gave the ring-opened product (**7**), which was then heated in methanol containing HCl to give the thienopyrrole (**8**). These results are analogous to those for 1,3-benzoxazepines[5] and 1*H*-1,3-benzodiazepines.[3]

Similarly, the thieno- (**9a**), furo- (**9b**), and pyrrolo-[3,2-*b*]pyridine *N*-imide (**9c**), upon irradiation, gave the corresponding fused 1*H*-1,2- (**10**) and 3*H*-1,3-diazepines (**11**), respectively (Scheme 2).‡



(9) (10) (11)

Scheme 2

a; X = S, R = Me
b; X = O, R = H
c; X = NMe, R = H

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‡ The yields of these new diazepines are as follows; (**10a**): 18%; (**10b**): 46%; (**10c**): 10%; (**11a**): 45%; (**11b**): 15%; (**11c**): 35%.

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