PHOTOCHEMICAL RING-EXPANSION OF ISOQUINOLINE AND THIENO[2,3-c]PYRIDINE N-IMIDES: FORMATION AND REACTIONS OF 1,3-DIAZEPINES

Takashi Tsuchiya, Hiroyuki Sawanishi, Michiko Enkaku, and Jyoji Kurita

School of Pharmacy, Hokuriku University,

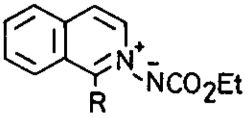
Kanagawa-machi, Kanazawa 920-11, Japan

Photolysis of the 1-substituted isoquinoline N-imides (1) resulted in ring-expansion with a two-step rearrangement via aziridine intermediates to give the previously unknown 1H-1,3-benzodiazepines (2), whereas photolysis of 1-unsubstituted isoquinoline N-imides gave only 1-aminoisoquinoline derivatives and no diazepines.

Further irradiation of the novel diazepine (2a) gave 1-ethoxycarbonyl-2-methylindole probably via the tricyclic valence isomer (3). Treatment of 2a with ethanol in the presence of acetic acid and then with water gave the ring-opened product (4), which was treated with hydrogen chloride to give 1-ethoxycarbonylindole. These results strongly support the structure of the new diazepine ring.

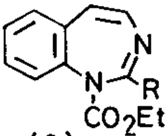
On the other hand, photolysis of the thieno[2,3-c]pyridine N-imide (5) gave two kinds of diazepines, the 1,3-thienodiazepine (6) and the 2,3-thienodiazepine (7). Some thermal and photochemical reactions of the new thienodiazepines (6 and 7) were examined.

The pathway for the formation of 6 and 7 will be discussed.

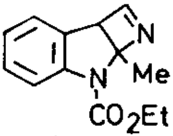


(1)

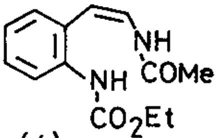
a: R=Me
b: R=CO_2Et



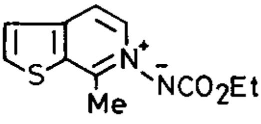
(2)



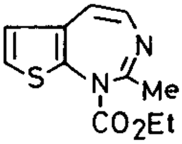
(3)



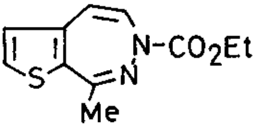
(4)



(5)



(6)



(7)