

REDUCTIVE PHOTOCYCLIZATION OF ENAMIDES

Takeaki Naito, Yukiko Tada, Yoshino Nishiguchi, Chiyomi Hashimoto,
Toshiko Kiguchi, and Ichiya Ninomiya.

Kobe Women's College of Pharmacy.

Motoyamakita, Higashinada, Kobe 658, Japan

In the course of our study on the photocyclization of enamides, we have undertaken investigation on the nature of the intermediate in enamide photocyclization using hydride reagent and as a result established the validity of the proposed intermediate and a new reductive photocyclization of enamides which was successfully applied to the synthesis of various types of heterocyclic compounds related to the isoquinoline alkaloids.

Contrary to the photocyclization of enamides under non-oxidative condition, irradiation of the enamide (3) in ether-methanol (20:1) at 5°-10° with a high-pressure mercury lamp through a Pyrex filter in the presence of sodium borohydride led to the formation of two hydrogenated lactams (4) and (5) and also led to the exclusive formation of the lactam (5) when acetonitrile-methanol (20:1) was used as the solvent. Upon irradiation of the enamide (3) in the presence of sodium borodeuteride, a quantitative incorporation of deuterium into the 4a-position of the photocyclized lactams (4a) and (5a) was observed and thus provided a strong support to the proposed mechanism of the photocyclization of enamides.

Reductive photocyclization of the enamide (11) prepared from 2-tetralone followed by reduction with lithium aluminum hydride afforded the benzo(f)quinolines (14) and (15), which have basic structures of the clavine alkaloids. Similarly, the enamides (16), (20) and (30), prepared from 3,4-dihydro-6,7-dimethoxy-1-methylisoquinoline and harmalan, were also irradiated in the presence of sodium borohydride to give the corresponding hydrogenated lactams (18), (22) and (31) in good yields respectively, of which the lactams (22) and (31) were readily converted into yohimban, alloyohimban, and alloyohimbone.

In addition to the previous results on non-oxidative and oxidative photocyclization, the above mentioned reductive photocyclization of enamides thus established that the enamide (3) for instance can be converted by irradiation into the corresponding dehydro-lactam (10), trans-lactam (7) or hydrogenated lactams (4) and (5) respectively by the choice of the irradiation conditions, either oxidative, non-oxidative or reductive condition.