A SYNTHETIC METHODOLOGY FOR THE SYNTHESIS OF OPTICALLY ACTIVE HETEROCYCLES BY ENAMIDE PHOTOCYCLIZATION

T. Naito, Y. Tada, and I. Ninomiya
Kobe Women's College of Pharmacy
Motoyamakita, Higashinada, Kobe 658, Japan

Existence of two reactive systems, iminium (A) and enolate (B) moieties, in the structure of a cyclic intermediate (C) of enamide photocyclization has drawn our interest on their use to asymmetric synthesis, which was visualized by the application of chiral circumstances to the photocyclization.

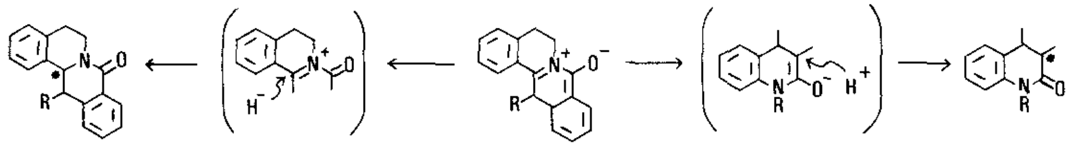
(1) Asymmetric Photocyclization Involving Enantioselective Reduction

Irradiation of the enamides, prepared from 1-alkyl-3,4-dihydroisoquinolines by simple benzoylation, in the presence of chiral metal hydride complex (reductive condition) at low temperature afforded the *optically active* 8-oxoberbines (1), thus demonstrating a potentiality of this cyclization as a useful synthetic tool for the asymmetric synthesis of heterocycles related to protoberberine alkaloids.

(2) Asymmetric Photocyclization Involving Enantioselective Protonation

Photocyclization of *N-acylanilides had been shown* to afford a mixture of cis- and trans-lactams, whose ratios being dependent on the solvent used. Expecting asymmetric protonation to an enolate moiety (B) of the cyclic intermediate (C), irradiation of the N-acylanilides in the presence of two molar amount of di-p-toluoyltartaric acid in benzene-ether (3:1) at 5-10°C was carried out and we found that the photocyclized products were the optically active quinolones (2) as a result of asymmetric protonation to the intermediate.

Thus, coupled with the previously developed non-oxidative, oxidative, and reductive photocyclizations, enamides are proved to be very potent synthons for the construction of various types of heterocycles particularly related to alkaloids.



R=H, Me (1) A C B (2)