CHEMISTRY OF EXCIPLEX AND ITS SYNTHETIC APPLICATIONS

SYNTHESIS OF OXINDOLES AND TETRAHYDROISOQUINOLONES AND PHOTOCLEAVAGE OF SULFONAMIDE BONDS

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Two kinds of potentially useful photoreactions via exciples, which is very important because it makes possible to occur "endothermic photosensitization" in classical energy transfer, are described.

I. Synthesis of Oxindoles and Tetrahydroisoquinolones

The efficiency of the intramolecular exciplex formation and the relative reaction rate of N-chloroacetyl-3,5-dimethoxyphenylalkylamines with various chain lengths were examined by quantum yield measurements of fluorescence quenching and relative disappearance, and were found to increase with shortening the alkyl chain. The apparent unreactivity of benzylamine derivatives for photocyclization, therefore, is attributed to the unfavorable conformation (trans-form) of the amide groups. Since the N-alkylation increases markedly the stability of the favorable cis-form, irradiation of N-alkylated benzylamine derivatives gave readily the corresponding cyclization products, tetrahydroisoquinolones. In the same manner, oxindoles were obtained by the photocyclization of N-alkylaniline derivatives.

II. Photochemical Cleavage of Sulfonamide Bonds.

The photolysis of N-tosyl-1-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline is known to give the corresponding 3,4-dihydroisoquinoline, 1,2,3,4-tetrahydroisoquinoline, and isoquinoline. This reaction was studied mechanistically, and was proved to proceed via the intramolecular exciplex between the electron-rich aromatic ring (donor) and the electron-deficient tosyl group (acceptor). An extension of this reaction to intermolecular photoreactions may provide a new general method for cleavage of usual sulfonamide bonds.