MECHANISM OF PHOTOCYCLIZATION OF N-CHLOROACETAMIDE DERIVATIVES HAVING ELECTRON-RICH AROMATIC RING

Osamu Yonemitsu, Yohmei Okuno, Naganori Numao, and Ken-ichi Hirao

Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060

Many novel heterocycles have been synthesized photochemically from N-chloroacetamide derivatives having electron-rich aromatic rings through various cyclizations owing to the variation of number and/or position of electron-donating substituents on the aromatic ring.

On the basis of detailed studies on solvent effects, pH dependence, fluorescence quenching and calculation of odd electron densities, we propose a common feature of the mechanisms in these photocyclizations.

In aqueous solvents, intramolecular electron transfer (photoionization) from the excited singlet state of an aromatic chromophore to the chloroacetyl moiety *via*. an exciplex, leads to the cleavage of the C-Cl bond. The resultant methylene radical couples readily with the aromatic cation radical to form cyclization products. The reactivity of the position on the aromatic ring to which the methylene radical couples corresponds to the odd electron density. The intermediate in phenol and indole derivatives able to release a proton are an aromatic neutral radical instead of the radical cation.

On the other hand, in organic solvents intramolecular energy transfer causes the homolytic cleavage of the C-Cl bond. The resultant methylene radical, after escape from a solvent cage, abstracts a hydrogen from solvents to yield reduction products. In the solvent cage, a new hydrogen abstraction reaction occurs to yield ten-membered lactams.