PHOTOREACTION OF IMIDE DERIVATIVES WITH A NITROGEN IN THEIR SIDE CHAINS: SYNTHESES OF MULTI-CYCLIC NITROGEN HETEROCYCLES BY THEIR PHOTOCYCLIZATION

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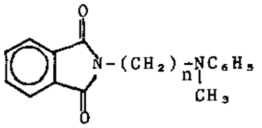
In our study of the imide photochemistry, we have introduced the working hypothesis of "donor-acceptor pair systems" in the photolysis of N-substituted phthalimides. We report here new examples of the photocyclization of such bichromophoric systems in which amino and amide groups play a role as the second chromophore.

Upon irradiation a homologous series of N-(ω-methylanilino)alkylphthalimides 1 with varying side chains (n= 1-6, 10, 12, 18) undergo regioselective remote photocyclization to give medium- to large-sized (up to 22 membered) diazacyclols. In the system of phthalimides with an aliphatic amino substituent 2, the photocyclization also occurred, by transfer of a hydrogen adjacent to nitrogen which is not limited to the γ or the δ position relative to the imide carbonyl, but in the far remote positions. However, in the amide system 3 similar reaction tendency was observed, but the hydrogen abstraction occurred only to the distance of the ζ position. For systematic comparison, the photochemistry of amide-containing succinimides 4, which are aliphatic counterparts of 3 was examind. In general, photolysis of 4 resulted in the products arising from initial γ-hydrogen abstraction, i.e., typical type II cyclization has occurred, indicative of different photochemical behavior from that of 3. One major distinction between aromatic and aliphatic cyclic imides is in that the aromatic imide system can be a good electron acceptor, which could favorably interact with a donor molecule such as an amino, or even to an amide group, in the course of photoreaction. In all cases a remarkable "cyclophilicity" of N-substituted imide derivatives was recognized and utilized for a synthesis of various multicyclic fused systems with two nitrogen atoms.



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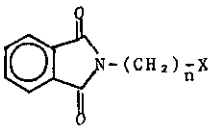
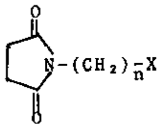


2 X= aliphatic amine
3 X= amide



4 X= amide