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# PHOTOCHEMICAL CLEAVAGE OF N-(HYDROPEROXYALKYL)PHTHALIMIDES BY INTRAMOLECULAR ENERGY TRANSFER

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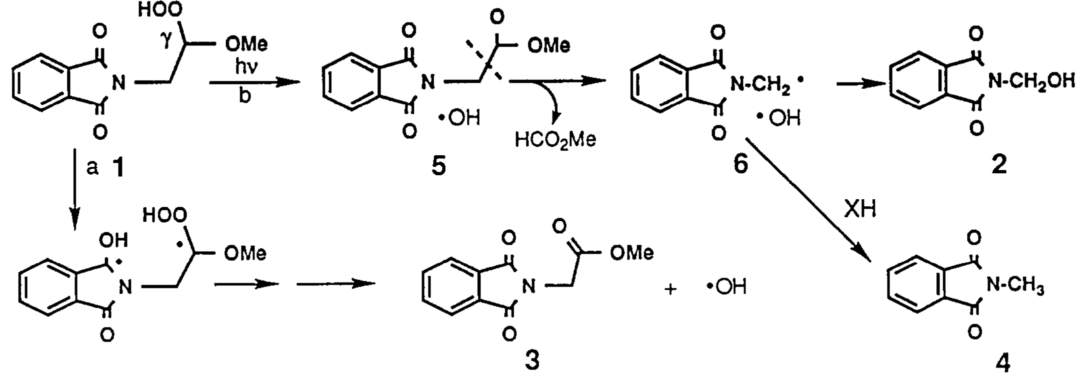
***Summary:*** *An unusual type of selective photocleavage of N-(hydroperoxyalkyl)phthalimides by intramolecular energy transfer has been described.*

We have been investigating the photochemistry of phthalimide derivatives possessing a hydroperoxyalkyl group in order to exploit an effective method for the photogeneration of hydroxyl radical (· OH) by long wavelength UV irradiation for the oxidation of biological systems.[1] We now wish to report an unusual type of selective photocleavage of N-(hydroperoxylalkyl)phthalimides initiated by intramolecular energy transfer.

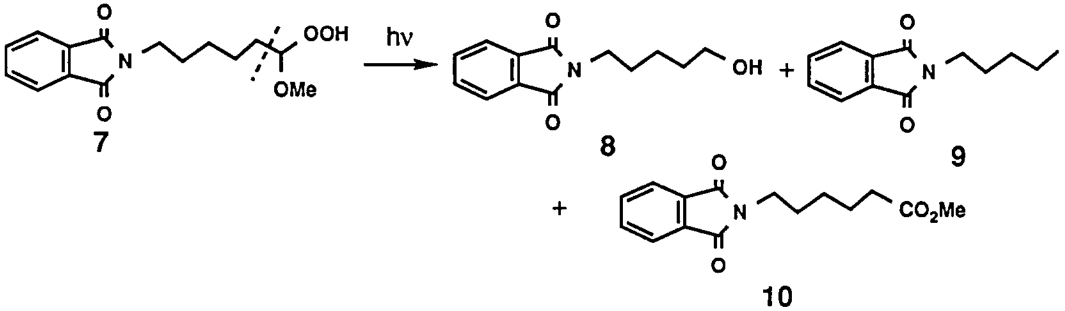
Photoirradiation (> 290 nm)[2] of **1** (0.2 mM) in acetonitrile under nitrogen gave the cleavage products **2** (72%) and methyl formate (79%) as major products together with minor amounts of **3** (5%) and **4** (3%). While **3** is apparently derived from γ-hydrogen abstraction by phthalimide carbonyl followed by O-O bond scisson with generation of · OH (path a),[1] the cleavage products **2** and methyl formate are assumed to arise from β-cleavage of the alkoxy radical **5** formed via the O-O homolysis of the hydroperoxy group (path b) (Scheme 1). In fact, irradiation of **1** in hydrogen-donating solvents such as THF provided **4** (30%) as a major product with a remarkably diminished yield of **2** (25%) along with the formation of **3** (8%), strongly suggesting the intermediary formation of **6** as the precursor of **2** and **4**. The radical **6** would then combine with hydroxyl radical in a solvent cage to produce **2**. A similar inhibitory effect

Scheme 1



on the formation of **2** was actually observed when the photolysis of **1** was conducted in the presence of dimethyl sulfoxide or adamantane as a hydroxyl radical scavenger.[3] All these results indicate that previously observed hydroxyl radical[1] is produced via the both pathways.

The formation of the cleavage products **2** and **4** from **1** is regarded as γ-cleavage type reaction in a sense of phthalimide photochemistry. While the photochemical α- and β-cleavage reactions of phthalimides are well precedented,[4] such a γ-cleavage reaction is very rare in phthalimide photochemistry.[5] In order to know the generality of this type of cleavage and to get insights into the possible involvement of intramolecular energy transfer process, we have examined the photochemistry of **7** having a remote hydroperoxy group. Irradiation of a highly diluted solution of **7** (0.05 mM) in acetonitrile under the same conditions resulted in a smooth conversion to give the cleavage products **8** (40%) and **9** (14%) together with **10** (28%), indicating that photoexcitation of phthalimide chromophore induces a selective cleavage of the remote C-C bond adjacent to the hydroperoxy group. The result is consistent with the mechanism involving intramolecular energy transfer from photoexcited phthalimide to the hydroperoxy group that is followed by O-O homolysis. The formation of **8** is again explained in terms of rapid coupling of the resulting alkyl radical with · OH generated in a solvent cage. The present results provide an intriguing example of the facile coupling of alkyl radical with · OH in a solvent cage, although an analogous alkly-alkoxyl radical coupling has been known in the photolysis of peresters.[6]



## References and Notes

1. I. Saito, M. Takayama, T. Matsuura, S. Matsugo, and S. Kawanishi, *J. Am. Chem. Soc.* **112**, 883 (1990).
2. Irradiated with a 100W high-pressure Hg lamp through a Pyrex filter at 0 °C. Under the conditions, incident light was absorbed only by the phthalimide chrompophore. $UV_{max}$ (acetonitrile) **1**, 286 nm (log ε 3.40); **7**, 288 nm (log ε 3.41).
3. Photoirradiation of **1** (0.1 mM) and adamantane (0.5 mM) gave **2** (32%), **3** (30%) and **4** (15%), whereas the photoirradiation in the presence of dimethyl sulfoxide produced **2** (35%), **3** (40%) and **4** (15%).
4. (a) P. H. Mazzocchi, Org. Photochem. **5**, 421 (1981) (b) J. D. Coyle, in "Synthetic Organic Photochemistry" W. D. Horspool ed., Plenum Press, 1984. (c) W. D. Horspool, in "Photochemistry in Organic Syntheses" J. D. Coyle ed., Royal Society of Chemistry, 1986.
5. One example is known for the γ-cleavage, see M. Tanabe, R. L. Dehn, and R. R. Bramhall, *J. Agr. Food Chem.* **22**, 54 (1974).
6. R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, **92**, 5175 (1970).

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