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PHOTOCHEMICAL REACTIONS OF N-ALKYL AND N,N-DIALKYLIMIDAZOLIDINETRIONES

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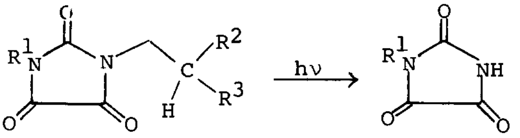
Summary: N-Akyl and N,N-Dialkylimidazolidinetriones undergo intramolecular hydrogen abstraction on irradiation to give elimination, intramolecular disproportionation, and cyclization products.

Imidazolidinetrione (parabanic acid) which possesses three carbonyl groups and two nitrogen atoms may be viewed as a composite of (i) urea and cis-glyoxal; (ii) a single carbonyl and cis-oxamide; (iii) one imide and one amide.[1c] Spectroscopic properties of imidazolidinetriones (1) have been studied extensively because of the unique structure.[1] However, photochemical reaction of these heterocycles has not been reported except for an ESR spectroscopic study on radicals formed by irradiation of 1 in water or isopropyl alcohol.[2] In relation to our previous studies on the photochemical reactions of α-di carbonyl compounds[3] and aroylureas,[4] we now report those of the heterocycles (1).



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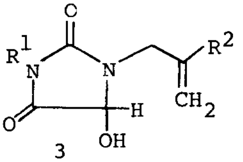

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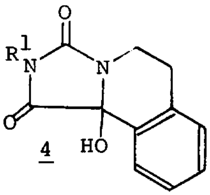

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a: R^1=Me, R^2=R^3=H
b: R^1=R^3=Me, R^2=H
c: R^1=H, R^2=R^3=Me
d: R^1=R^2=R^3=Me
e: R^1=R^2=H, R^3=Ph
f: R^1=Me, R^2=H, R^3=Ph
g: R^1=Ph, R^2=R^3=Me
h: R^1=R^3=Ph, R^2=H,

a: R^1=Me
c: R^1=H

b: R^1=Me, R^2=H
c: R^1=H, R^2=Me
d: R^1=R^2=Me

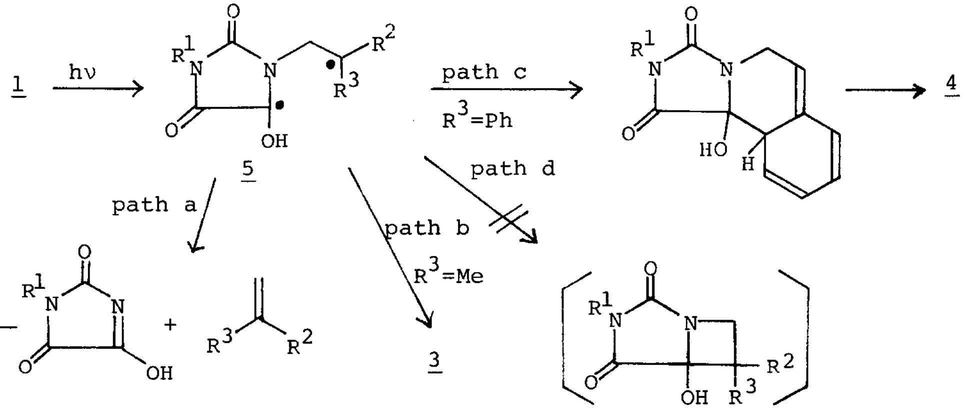
e: R^1=H
f: R^1=Me

Photoreaction of 1 (yield %)

	2	3	4
1a	28	-	-
1b	trace	46	-
1c	0	73	-
1d	0	73	-
1e	0	-	87
1f	0	-	93

The results of photoreactions of imidazolidinetriones (1) varies remarkably with the substituents on the nitrogens. When N-ethyl-N-methylimidazolidinetrione (1a) in acetonitrile was irradiated with a high pressure mercury lamp under argon through a Pyrex filter,[5] N-methylimidazolidinetrione (2a) was obtained. Photolysis of N-propyl and N-isobutyl derivatives (1b, 1c and 1d) gave the corresponding intramolecular disproportionation products (3b, 3c and 3d) respectively. On the other hand, irradiation of N-phenylethyl derivatives (1e and 1f) gave tricyclic compounds (4e and 4f) in high yields, while N-phenyl derivatives (1g and 1h) were inert toward photolysis. The structures of the products (3 and 4) were determined on the basis of elemental analyses and spectral data.[6] The structure of 3d was further confirmed by the fact that oxidation of 3d with chromic trioxide in pyridine and subsequent hydrogenation of the resulting product afforded 1d.

The formation of the three types of products can be reasonably explained in terms of the 1,4-diradical intermediate (5) formed by γ-hydrogen abstraction by the α-dicarbonyl group (Scheme). Cleavage of the N-CH$_2$ bond followed by ketonization gives 2a (path a), whereas 1,5-hydrogen migration of 5 yields 3 (path b). Bond formation between the radical center at the ring and the ortho position of the phenyl group, and subsequent aromatization afford 4 (path c). Since the photoreaction of 1d was sensitized by acetone and efficiently quenched by 1,3-pentadiene, the hydrogen abstraction is presumed to proceed from the n,π^* triplet state as with photoreaction of α-diketones.[7] It has been reported that the lowest triplet (T_1) state of N-alkylimidazolidinetriones is highly localized on the dicarbonyl residue and is of n,π^* type.[1a] The efficiency of photoreactions of the N,N-dialkyl derivatives (1d and 1f) was similar to that for the N-alkyl derivatives (1c and 1e) in spite that the T_1 state of N,N-dialkylimidazolidinetriones is a mixed $n,\pi^*/\pi,\pi^*$ state.[1a]



Although reactions similar to path a (type II cleavage) and path b (disproportionation) are known to occur in photolysis of cyclic imides,[8] those involving participation of a phenyl group attached to a radical center of a 1,4-diradical (as with path c) are hitherto unknown in the photochemistry of cyclic imides[9] and α-dicarbonyl compounds, to our best knowledge. This cyclization (path c) is presumed to be synthetically useful.

It is worth emphasizing that none of the imidazolidinetriones (1a-f) undergo type II cyclization. This finding is of particular interest in view of the fact that both cyclic imides[7] and α-diketones[9] predominantly undergo type II cyclization on irradiation. Furthermore, photolysis of 1c-f gave neither type II cyclization nor cleavage products, and the cleavage took place efficiently only in the case of <u>1a</u> which can not undergo the other two reactions (path b and path c). These results indicate that the usual type II reactions are unfavorable processes for the 1,4-diradical (<u>5</u>). The unfavorableness of the type II cleavage of <u>5</u> is explainable in terms of its geometry. It is widely accepted that efficient cleavage of a 1,4-diradical requires overlap of the σ-bond to be broken with both singly occupied p-orbitals.[10] However, conjugation of one of the radical centers of <u>5</u> with the adjacent carbonyl group (and with the nitrogen) holds the radical p-orbital perpendicular to the N-CH_2 bond. Meanwhile, the reason why type II cyclization did not occur in the photolysis of the imidazolidinetriones is not clear at present. The nonreactivity of the N-phenyl derivatives (<u>1g</u> and <u>1h</u>) may be ascribable to localization of the excitation on the N-phenyl component rather than the α-dicarbonyl group.[11]

Although many reports have been published on photochemical hydrogen abstraction reacrions of α-dicarbonyl compounds,[12] all of them involve hydrogen abstraction by ketone carbonyl groups. The present reaction provides the first example of hydrogen abstraction by non-ketonic carbonyl groups in the photochemistry of α-dicarbonyl compounds.

In conclusion, N-alkyl and N,N-dialkylimidazolidinetriones undergo photochemical hydrogen abstraction as cyclic imides and α-diketones, but the behavior of the 1,4-diradical (<u>5</u>) formed by the abstraction is considerably different from that of diradicals from cyclic imides.

<u>References and Notes</u>

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4) H. Aoyama, M. Sakamoto, M. Ohnota, and Y. Omote, Chem. Lett., 1983, 1905.

5) The imidazolidinetriones show the n,π^* absorption bands at 310-315 nm, see

reference 1a.

6) 4f: m.p. 127-8°C; IR (KBr) 3320, 1770, 1690 cm^{-1}; ^{1}H-NMR ($CDCl_3$) 2.5-3.1 (m, 2H, C-CH_2), 2.95 (s, 3H, CH_3), 3.2-3.55 and 4.0-4.3 (each m, each 1H, N-CH_2), 5.0 (br. s, 1H, OH), 6.9-7.4 (m, 3H, aromatic), 7.7-8.0 (m, 1H, aromatic); ^{13}C-NMR ($CDCl_3$) 24.8 (q), 27.7 (t), 35.2 (t), 81.8 (s), 127.2 (d), 127.5 (d), 128.9 (d), 129.5 (d), 131.2 (s), 134.2 (s), 155.5 (s), 172.4 (s).

7) P. J. Wagner, R. G. Zepp, K Liu, M. Thomas, T. Lee, and N. J. Turro, J. Am. Chem. Soc., **98**, 8125 (1976), and references cited therein.

8) (a) Y. Kanaoka, Y. Migita, K. Koyama, Y. Sato, H. Nakai, and T. Mizoguchi, Tetrahedron Lett., **1973**, 1193 (b) Y. Kanaoka and Y. Hatanaka, J. Org. Chem., **41**, 400 (1976).

9) It is known that photolysis of N-phenylethylphthalimide gives only a complex mixture of minor products: Y. Kanaoka and Y. Migita, Tetrahedron Lett., **1974**, 3639.

10) (a) P. J. Wagner, Acc. Chem. Res., **4**, 168 (1971). (b) P. H. Mazzocchi, Org. Photochem., **5**, p 447 (1981).

11) Triplet energies of imidazolidinetriones are 78-81 kcal (reference 1a), while that of aniline is 77 kcal (S. L. Murov, "Handbook of Photochemistry", Mercel Dekker, New York, 1973).

12) For photoreactions of α-diketones, see reference 7. For those of α-oxoesters, see: (a) E. S. Huyser and D. C. Neckers, J. Org. Chem., **29**, 276 (1964). (b) P. A. Leermakers, M. E. Ross, G. F. Vesley, and P. C. Warren, ibid., **30**, 914 (1965), and references cited therein. For those of α-oxoamides and imides, see reference 3.

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