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PHOTOINDUCED REACTIONS. LXVII.
PHOTOSENSITIZED OXYGENATION OF N-SUBSTITUTED 1,2,3,4-TETRAHYDROCARBAZOLES 1)

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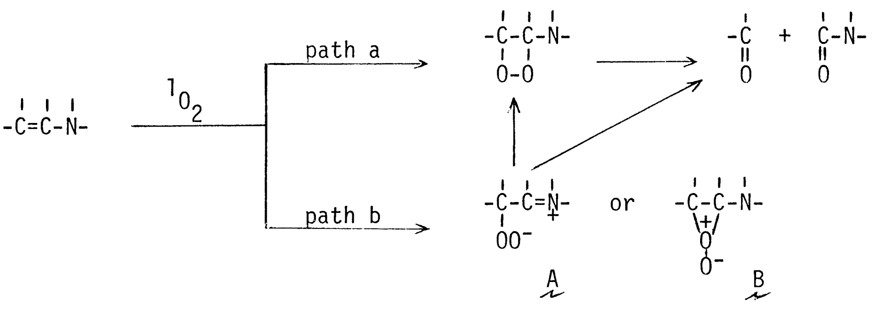
Rose bengal-sensitized photooxygenation of N-methyl- (**1a**), N-methyl-6-nitro- (**1b**), and N-acetyl- (**1c**) 1,2,3,4-tetrahydrocarbazoles was investigated. The N-methyl derivatives underwent oxidative cleavage of the enamine double bond to give exclusively **2**, whereas the N-acetyl derivative in water-containing solvents gave predominantly **3**, possibly *via* a zwitterionic peroxide intermediate.

The dye-sensitized photooxygenation of tertiary enamines undergoes oxidative α,β-cleavage to carbonyl fragments. This reaction has been interpreted as 1,2-cycloaddition of singlet oxygen to the electron-rich double bond followed by thermal decomposition of a dioxetane intermediate [eq. (1), path a],2-4) although the dioxetane formation was not experimentally determined. However, an alternative mechanism [eq. (1), path b] involving a zwitterionic peroxide such as **A** and **B** cannot be ruled out for the α,β-cleavage of tertiary enamines and of other electron-rich olefins.3) Some evidence for the formation of such a zwitterionic peroxide in the photosensitized oxygenation of fully N-alkylated uric acids was previously reported,4,5) and we report here experimental results which may support it.



(1)

Rose bengal-sensitized photooxygenation of N-methyl-1,2,3,4-tetrahydrocarbazole (**1a**) in methanol at room temperature under irradiating with a tungsten-bromine lamp (visible light) resulted in the absorption of one mole equivalent of oxygen to give **2a**6) in 90% yield. Similar results were obtained when the photooxygenation was carried out in acetone at room temperature (95% yield) and in methanol-pyridine (50:1) at 0°C (95% yield). Similar photosensitized oxygenation was carried out with N-methyl-6-nitro-1,2,3,4-tetrahydrocarbazole (**1b**)7) in acetone, which is considered to be less electron-rich than **1a** because of the substitution with an electron-withdrawing nitro group. As expected, it underwent slower cleavage to give **2b**8) (45%) and the recovered starting material (43%).

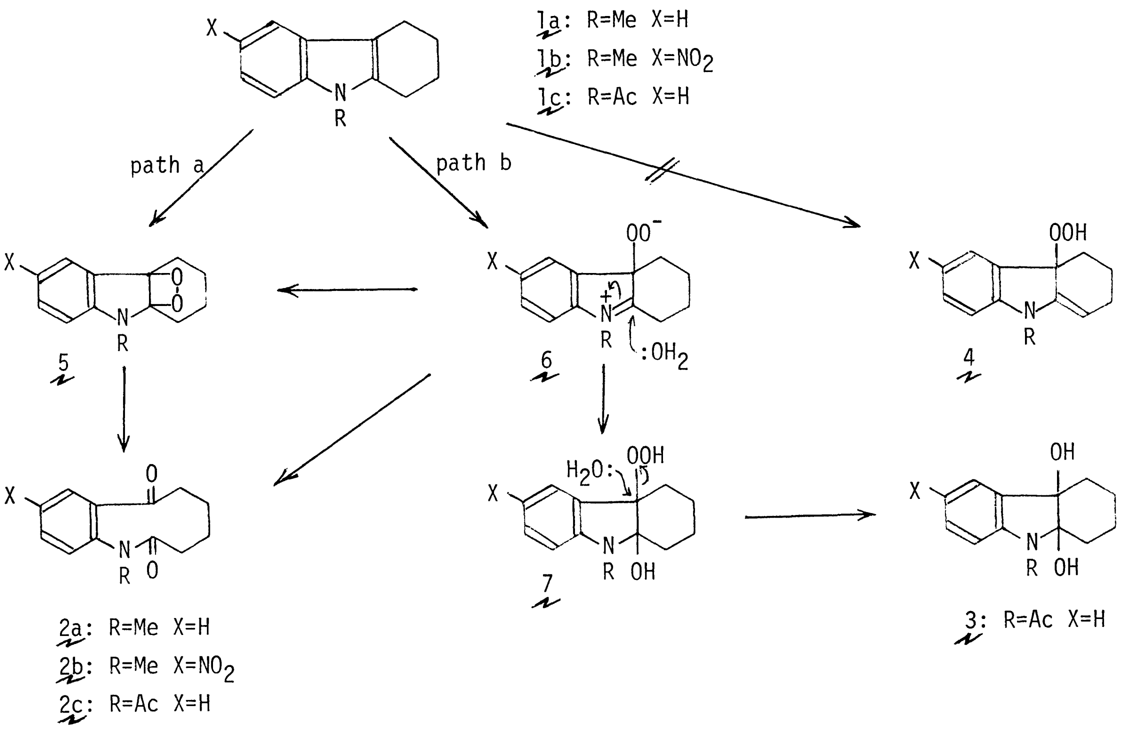
On the other hand, photosensitized oxygenation of N-acetyl-1,2,3,4-tetrahydrocarbazole (**1c**) in methanol under similar conditions resulted in the formation of a cleavage product **2c** (57%) and a dihydroxylated product **3** (8%).9) When the photooxygenation was carried out in acetone containing water, the yield of **3** increased up to 54%, indicating that water is essential for the formation of **3**.

It should be noted that in every case the formation of an allylic hydroperoxide such as **4** could not be detected. Although such an allylic hydroperoxide has been known to undergo cleavage by acid catalysis giving carbonyl fragments, possibly via a dioxetane intermediate,10) the exclusive formation of **2a** in the photooxygenation of **1a** in a basic solvent system (methanol-pyridine) suggests that the oxidative cleavage of **1a**, **1b**,and **1c** may not proceed through the allylic hydroperoxide **4**.

The results could be rationalized by a dual mechanism involving a dioxetane **5** [eq. (1), path a] and a zwitterionic peroxide **6** [eq. (1), path b]11) as the initial product in the addition of singlet oxygen to these tetrahydrocarbazoles **1**, as depicted in Scheme 1. The zwitterionic peroxide **6** may undergo cyclization to **5**, which gives rise to **2**, and hydrolysis to **7** which is further hydrolyzed to give **3**. A direct cleavage of **6** to **2**, presumably involving a four-centered transition state, may not be ruled out because no definite evidence is available for the formation of a dioxetane from enamines.2-4)

Although an alternative pathway involving the hydrolysis of the dioxetane **5** to **7** can be envisioned, it may be discounted on the following grounds: i. e., thermolysis of dioxetanes in various solvents gives exclusively carbonyl fragments12-15) and only a strong nucleophile such as hydroxide and azide anions can decompose a dioxetane to products other than carbonyl fragments.16) Although the photosensitized oxygenation of an N-acetylenamine, N-acetyltryptophan, is known to give products cleaved at the double bond,17) the role of the acetyl group for the predominant formation of **3** is unknown.18)

Scheme 1



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5) Other investigators also suggested the formation of such a zwitterionic peroxide in the photosensitized oxygenation of certain enamine systems.[2a,2c,2e)]

6) The product 2a was identical with an authentic sample. [L. J. Dolby and D. L. Booth, J. Amer. Chem. Soc., 88, 1049 (1966).]

7) This compound was synthesized by applying the known method by Noland et al. [W. E. Noland, L. R. Smith and K. R. Rush, J. Org. Chem., 30, 3457 (1965).]

8) The structure 2b was assigned on the basis of its spectral properties analogous to those of 2a: 2b; mp 134°C; λ_{max}^{EtOH} 290nm (ε 5450); ν_{max}^{nujol} 1695, 1650, 1520, 1350cm^{-1}; $\tau(CDCl_3)$ 1.50-2.67m (3H), 6.72s (3H), 7.10-8.10m (8H); m/e 262. Satisfactory microanalyses were obtained for all new compounds.

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11) A peroxirane intermediate[3)] [eq. (1), B] may be a candidate for such a zwitterionic peroxide.

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18) It may be suggested that the zwitterionic peroxide 6 is stabilized only in the case of 1c, presumably by the N-acetyl group, because the rose bengal-sensitized photooxygenation of 1a in acetone containing water gave 2a in 90% yield but no appreciable amount of product of type 3. The authors are indebted to Mr. Sho Abe for carrying out this experiment.

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