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EVIDENCE FOR THE FORMATION OF OXAZIRIDINES DURING THE IRRADIATION OF OXIMES[1]

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Compared to the photochemistry of ketones, that of oximes has not been studied so extensively and a few papers dealing with the photoexcited state (2) and mode of the photoreaction of oximes, e.g., the syn-anti isomerization (3), the Beckmann type rearrangement leading to carboamides (2c, 4), and the formation of nitriles (5) have been reported.

We have discovered a new photoreaction of oximes, the formation of oxaziridines, which was suggested without evidence by de Mayo as an intermediate in the photoreaction of benzaldoxime to benzamide (6). We chose oxime (I) of 1,1-dimethyl-2-naphthalenone (II) because of its absorption maximum above 300 mμ and of stability of the expected photoproducts. Although there are two geometrical isomers of I, the syn-form (Iα), m.p. 103-4°, and anti-form (Iβ), m.p. 133-5° (7), irradiation induced interconversion between the two isomers.

When a solution of the oxime (Iα) was irradiated in a Pyrex vessel using a high pressure mercury lamp (Toshiba H400-P), the absorption maximum of Iα at 307 mμ was replaced by that of a photoproduct (III) at 274 mμ. Although the photoproduct (III) seems to be stable when it is in dilute solution (less than 0.01 M) (8), it failed to isolate III upon evaporation of the solvent. Evaporation of the irradiated solution of Iα resulted in decomposition of III, and afforded an unsaturated ketone (II)(yield 54 %), a saturated ketone (IV)(6.4 %), a carboamide (V)(9), m.p. 141-3° (4 %), and recovered oximes (Iα and Iβ)(8 %) accompanied with nitrogen and hydrazine. On the other hand, when the irradiated solution was hydrogenated immediately in the presence of Pd-C, the saturated ketone (IV)(27 %), the carboamide (V)(5 %) and a saturated alcohol (VI), m.p. 88-9° (39 %), were

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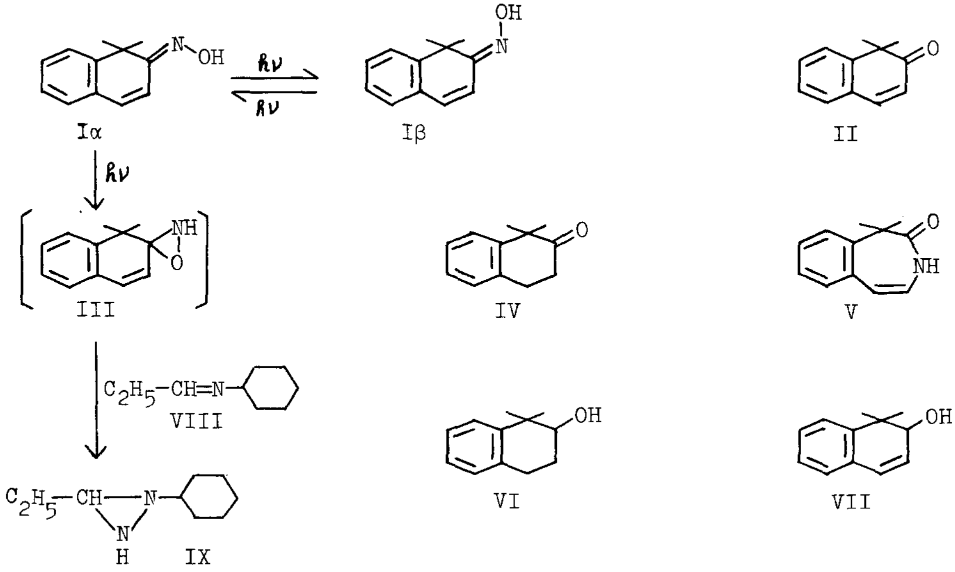
obtained. Reduction of the solution with sodium borohydride yielded an unsaturated alcohol (VII), m.p. 59-61° (50 %). After acidification with acetic acid, refluxing of the benzene solution containing III regenerated Iα (43 %) and Iβ (40 %). These facts suggest that III is an oxaziridine derivative.



The decisive evidence for the structure of III is as follows. After irradiation of a methanol solution of Iα for 1.5 hr, treatment with potassium iodide liberated 0.82 equivalent of iodine accompanied with the formation of II, indicating the yield of III being around 80 % (10). Reaction of the irradiated solution of Iα with Schiff base (VIII) afforded a diaziridine (IX)(25 %) (11) and the unsaturated ketone (II)(63 %). These reactions are exactly the same as those reported for oxaziridine derivatives (12).

The formation of the oxaziridine (III) from the oxime (Iα) seems to proceed via a singlet state, because no quenching effect of oxygen or piperylene was observed. It was found that the formation of III is faster in protic solvents such as methanol and 2-propanol than in aprotic solvents such as acetonitrile, benzene and cyclohexane. This fact suggests that a protonation may be involved in some step of the rearrangement or the oxaziridine-formation may proceed via a polarized excited state (13).

Irradiation of benzalacetone-oxime (XI) was carried out under the same condition as for Iα, in which case the UV absorption maximum of XI at 283 mμ disappeared and a new absorption maximum appeared at 257 mμ, but this new absorption band was labile compared to that of III. After irradiation of XI for 3 hr in methanol, treatment of the irradiated solution with potassium iodide liberated 0.5 equivalent of iodine accompanied with benzalacetone (XIII) and recovered oxime (XI), and this indicated that the oxaziridine (XII) was formed in about 50 % yield. Without treating with potassium iodide, evaporation of the irradiated solution of XI afforded benzalacetone (XIII), amides (XIVa) m.p. 106-8°, and (XIVb) m.p. 63-4°, and 4-phenylbutane-2-one (XV). As shown in Table 1, the yield of the photoproducts depended on the conditions used. The results in the Table seem to be compatible with the assumption proposed by de Mayo that amides would be formed through oxaziridine as an intermediate (6). However, this assumption is still in doubt, because further irradiation or heating of the methanolic solution containing III did not result in increased formation of amide (V)(14).

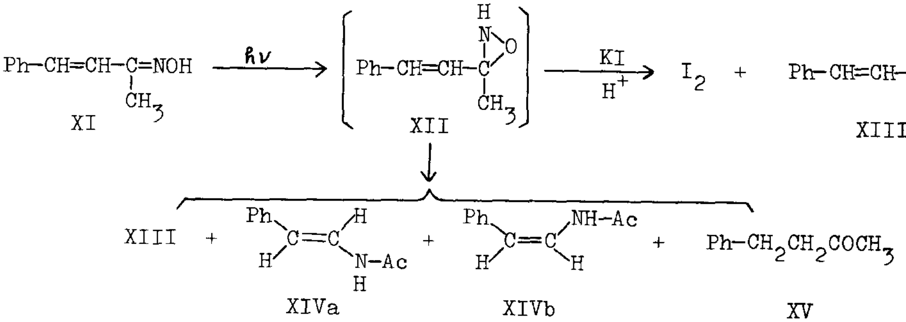


Table 1

solvents	irradiation time (hr.)	yield (%)			
		XIII	XIVa	XIVb	XV
MeOH	9	30	2.4	3.6	ca. 3
MeOH	24	10	5.6	14	trace
AcOH	24	6	16	40	-

Whether the formation of oxaziridines from oximes is a general photoreaction or not is of interest. In order to clarify this problem, we have investigated the photochemistry of the other oximes shown in Table 2. Although the result is preliminary, it was found that saturated ketoximes such as cyclohexanone-oxime, upon irradiation with low pressure mercury lamp in a quartz vessel, could liberate iodine from potassium iodide similar to as the oximes (I) and (XI). The corresponding ketones or aldehydes were obtained in considerable yield in the cases cited in Table 2. We are undertaking a more detailed study in this series of compounds.

Table 2

Oxidizing character of the irradiated solution of oximes*

oximes	high pressure Hg-lamp (Pyrex)	low pressure Hg-lamp (quartz)
cyclohexanone	-	+
2-cyclohexenone	-	+
benzaldehyde	-	+
acetophenone	+	+

*The irradiation were carried out in MeOH. The positive sign (+) indicates that treatment of the irradiated solution with KI liberated more than 0.1 equivalent of I_2 (based on the oxime).

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6. Ref. 4 and Solvey Institute 13th Chemistry Conference, " Reactivity of Photo-excited Organic Molecule" Interscience Publishers, New York, N.Y. 1967, p 320.
7. The structures of these two isomers (1α and 1β) were established by nmr spectral data. All new compounds in this paper gave satisfactory elemental analyses.
8. The UV spectrum of III did not change when a methanolic solution (0.01 M) of III was allowed to stand overnight at room temperature or a benzene solution (0.01 M) of III was refluxed for 1.5 hr.
9. The structure of V was established by nmr spectroscopy; (in $CDCl_3$) τ 8.48 (6H s), 3.95 (1H d.d. J=9.5 and J=4.5 Hz), 3.71 (1H d.d. J=9.5 and J=ca 2 Hz), 2.5-2.9 (4H m), 1.50 (1H br. d. J=4.5 Hz).
10. When benzene was used as a solvent, 0.64 equivalent of iodine was liberated.
11. E. Schmitz, R. Ohme and S. Schramm, Ber., 97, 2521 (1964).
12. a) W.D. Emmons, J. Am. Chem. Soc., 79, 5739 (1957). b) E. Schmitz in " Advances in Heterocyclic Chemistry" Vol II, ed. by A.R. Katritzky, Academic Press, New York, N.Y., 1963, p 92.
13. The photochemical formation of III from I reminds us that the photolysis of nitrones give oxaziridine derivatives. For example; J.S. Splitter and M. Calvin, J. Org. Chem., 23, 651 (1958). K. Shinzawa and I. Tanaka, J. Phys. Chem., 68, 1205 (1964).
14. The formation of the amide (V) was increased by further irradiation only in acetic acid.