Tetrahedron Letters No. 26, pp 2689 - 2692, 1972. Pergamon Press. Printed in Great Britain.

PHOTOINDUCED REACTIONS. LXII.

PHOTOCHEMICAL REACTION OF α-NITROEPOXIDES[1)]

I. Saito, M. Takami, T, Konoike and T. Matsuura

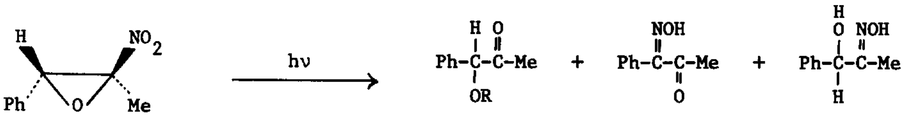
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

(Received in Japan 19 May 1972; received in UK for publication 23 May 1972)

Photochemical transformation of small-ring carbonyl compounds including α,β-epoxyketones has been extensively investigated.[2),3)] However, no photochemical reaction of nitro compounds attached to a small ring has been reported. We now wish to report the photochemical behavior of α-nitroepoxides showing marked solvent dependence.

In methanol 1-phenyl-2-methyl-2-nitrooxirane 1 was slowly converted to a methanol adduct 2a even in the absence of light[5)], whereas in other solvents such as isopropyl alcohol or ether 1 was quite stable in the absence of light. We employed, therefore, isopropyl alcohol or ether as a solvent for the photochemical reaction of 1. When 1 (λ_{max} 290 nm (ε 450), 230 nm (ε 4500)) was irradiated by high-pressure mercury lamp (Pyrex filter) in isopropyl alcohol under nitrogen atmosphere at room temperature, three products 2b[6)] (31 %), 3[7)] (41 %), and 4[4)] (11 %), were obtained, the structure of which were confirmed by their synthesis.

Irradiation of 1 in ether led to the exclusive formation of 4. The results of the photolysis of 1 in a mixture of isopropyl alcohol and ether in different ratio are shown in the Table. On the other hand, 1 was found to be stable to photolysis in t-butylalcohol, benzene, acetone and acetonitrile. These results indicate that an unhindered protic solvent is essential to the formation of 2 and 3, whereas the hydrogen-donationg ability of solvents could be respondible for the formation of 4.



1

2 a: R=Me
b: R=i-Pr

3

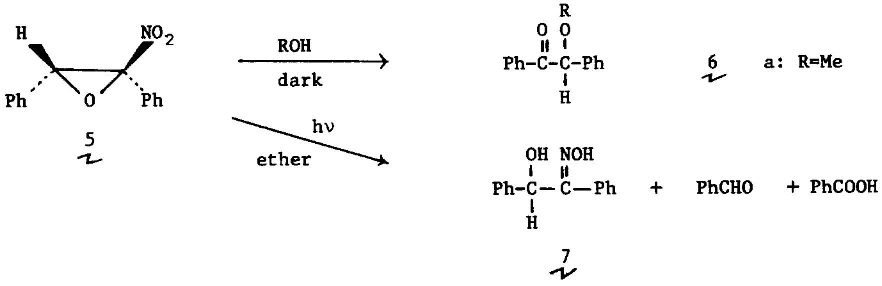
4

Table Photolysis of 1 in various solvents

Solvent	Yield of product (%)a)			Recovered 1 (%)a)
	2	3	4	
MeOH	85	-	-	12
i-PrOH	31	41	11	17
i-PrOH : Et$_2$O (9:1)	20	25	15	39
i-PrOH : Et$_2$O (1:1)	8	-	31	57
i-PrOH : Et$_2$O (1:9)	-	-	30	67
Et$_2$O	-	-	20	80

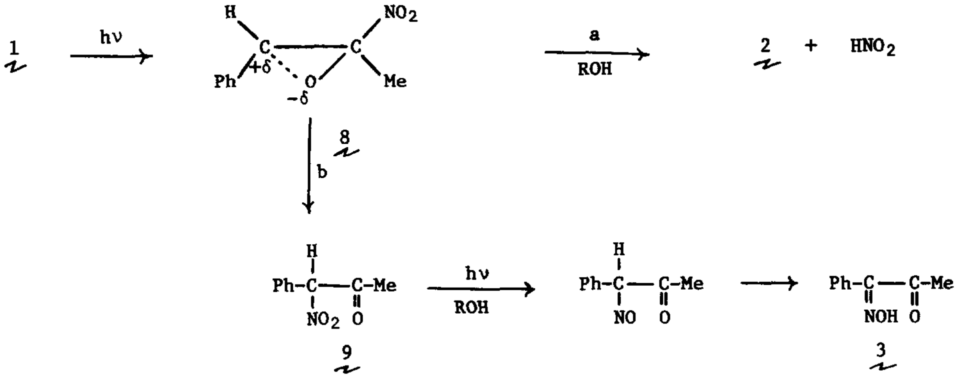
a) Determined by n.m.r.

1,2-Diphenyl-2-nitrooxirane (5)4) was unstable in the presence of an alcohol in the dark to give rise to 68), but stable in ether. Irradiation of 5 (λ_{max} 290 nm (ε 800), 232 nm (ε 6000)) in ether under similar conditions gave a complex mixture of products from which benzoin oxime 7 (35%), benzaldehyde (15%) and benzoic acid (11%) were isolated.



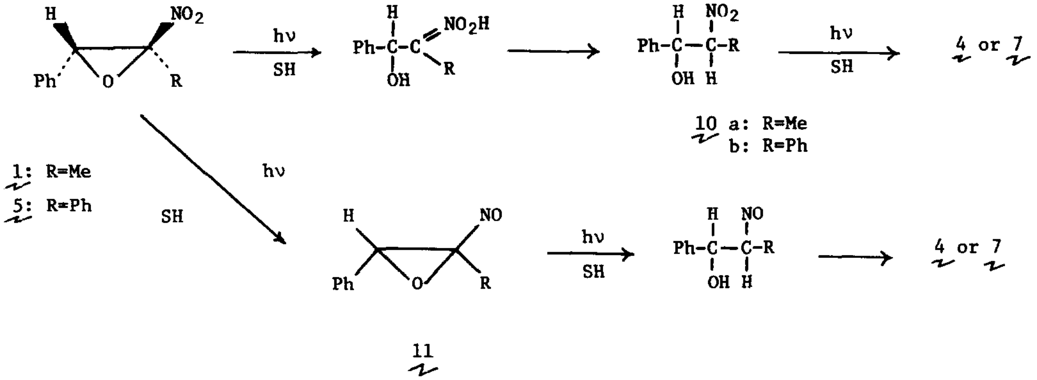
The formation of 2 and 3 may be explained by a mechanism (Scheme 1) involving a polar intermediate 8, which is derived from the excited state of 1 9) presumably with assistance by a proton of the solvent alcohol. The intermediate 8 may react with an alcohol10) to give 2 with the elimination of nitrous acid13) (path a) or may rearrange to 9 by 1,2-shift of the nitro group14), which is followed by photoreduction to give rise to 3 (path b). Supporting this mechanism, nitroketone 94) was found to be rapidly converted to 3 upon photolysis under the conditions.

Scheme 1



Although the mechanism of the photoreduction of 1 and 5 in ether leading to 4 and 7, respectively remains to be clarified, it is clear that 10a[4] and 10b[15], which were found to be unreactive to photolysis in ether, could not be a possible intermediate for the formation of 4 and 7, respectively. It is, therefore, probable that another possible intermediate, nitrosoepoxide 11[16] may account for the formation of 4 and 7 as shown in Scheme 2.

Scheme 2



REFERENCES

1. Part LXI; T. Matsuura and Y. Ito, Chemistry Letters, submitted.
2. A. Padwa, "Organic Photochemistry", ed. O. L. Chapman, vol. 1, p. 91, Marcel Dekker, Inc., New York (1967).

3. A. Padwa, *Accounts Chem. Res.*, **4**, 48 (1971).
4. H. Newman and R. B. Angier, *Tetrahedron*, **26**, 825 (1970).
5. The rate of solvolysis of **1** by methanol was remarkably accelerated by irradiation.
6. V. Auwers and L. Müller, *Liebigs Ann. Chem.*, **524**, 155, 162, 170 (1936).
7. O. L. Chapman, *Pure Apple. Chem.*, **9**, 585 (1964).
8. I. Wier, *J. Chem. Soc.*, **91**, 1391 (1905).
9. The formation of **2** and **3** was not affected by adding piperylene, whereas the formation of **4** in ether was efficiently quenched by piperylene.
10. Photochemical polar addition of an alcohol to epoxides has been reported.11),12)
11. K. Tokumaru, *Bull. Chem. Soc. Japan*, **40**, 242 (1967).
12. R. C. Petterson, C. S. Irving, A. M. Khan, G. W. Griffin, and I. M. Sarkar, 158 th National Meeting of the American Chemical Society, September, 1969, New York, ORGN-10.
13. The liberation of nitrogen oxides was confirmed by trapping with an acetic acid solution of sulfanilic acid and N,N'-dimethylnaphthylamine.
14. The 1,2-shift of an alkyl group is well established in the photochemistry of α,β-epoxyketones.2),3)
15. F. G. Bordwell and E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 2322 (1962).
16. Attempts to synthesisze this compound were unsuccessful so far.