Tetrahedron Letters No. 36, pp 3155 - 3158, 1975. Pergamon Press. Printed in Great Britain.

NITRO-NITRITE REARRANGEMENT AND INTRAMOLECULAR CYCLOADDITION IN THE PHOTOCHEMISTRY OF NITRO-OLEFINS[1]

Isao Saito*, Masaaki Takami, and Teruo Matsuura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University
Kyoto 606, Japan

(Received in Japan 24 June 1975; received in UK for publication 24 July 1975)

In 1964 Chapman, et al. have reported a photorearrangement of α,β-unsaturated nitro-olefins to α-oximino ketones.[2] Thereafter, a large number of examples of the nitro to nitrite rearrangement have been shown in the photochemistry of nitro-olefins[3] and of nitro aromatic compounds,[4] while the mechanism of the reaction, especially multiplicity of the excited state of the nitro group, has not been fully understood. More recently, an intramolecular cycloaddition of a nitro group to a carbon-carbon double bond has been suggested for the photochemical double bond cleavage of cis-α,4-dinitrostilbene.[5] As part of our studies on the photochemistry of nitro compounds,[6] we have reinvestigated the photochemical reactions of a series of substituted (E)-β-methyl-β-nitrostyrenes in some detail and found that the nitro to nitrite rearrangement and the intramolecular cycloaddition are taking place competitively from different excited states. Chemical trapping of the intermediates in the reaction is also described.

It has previously been reported that irradiation of β-methyl-β-nitrostyrene (1a) gives α-oximino ketone 2a as a sole product.[2] In contrast, we found that irradiation of nitrostyrenes having electron-withdrawing substituents yields both the corresponding α-oximino ketones and substituted benzaldehydes. For example, when a solution of (E)-4-chloro-β-methyl-β-nitrostyrene (1b) (1.11×10^{-2} M) in acetone was irradiated (Pyrex filter, 100 W high pressure mercury lamp) under nitrogen atmosphere for 5 hr, α-oximino ketone 2b[7,8] (65 %) and p-chlorobenzaldehyde (3b) (14 %) were obtained.[9] Under similar conditions, p-substituted nitrostyrenes (1a~f) gave the corresponding α-oximino ketones 2a~f and substituted benzaldehydes 3a~f. The product ratio 3/2 is shown in Table. We also observed that there has been no significant solvent dependency on the product ratio 3/2.[10] During irradiation and work-up process, α-oximino ketone 2 was not be converted to 3, indicating that 3 may be formed from a different precursor. If 3 may arise from the N-oxide intermediate 4 (path b), nitrile oxide 5 should be formed in the

reaction. In fact, irradiation of a solution of 1d (2.4×10^{-2} M) and methyl acrylate 6 (0.29 M), a well known 1,3-dipolarophile to nitrile oxide,[11] in acetonitrile under nitrogen gave isoxazoline 7 in 12 % yield (90 % based on 3d) (Scheme I).

Scheme I

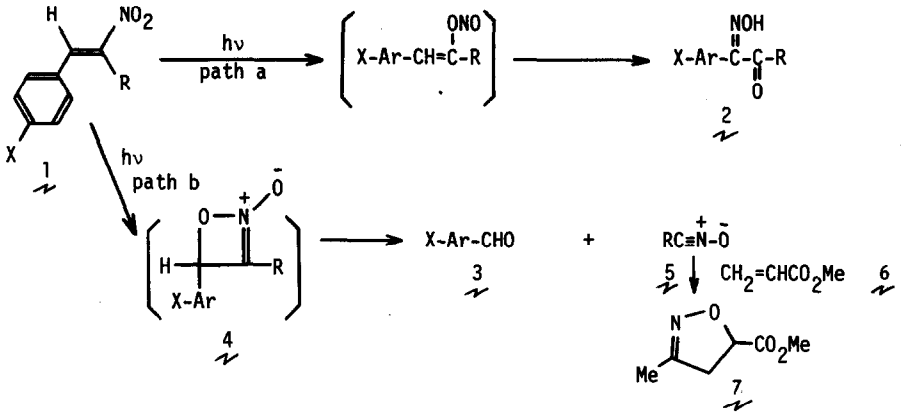


TABLE. Products of Photoreaction of Substituted β-Nitrostyrenes

Nitrostyrene	X	R	Solvent	Yield of Products %[a] 2	3	Product Ratio[b] 3/2
1a	H	Me	Acetone	80	6	0.08
1b	Cl	Me	Acetone	65	14	0.22
1c	OMe	Me	Acetone	89	3	0.04
1d	NO_2	Me	Acetone	61	15	0.28
1e	H	Et	Benzene	78	4	0.06
1f	NO_2	Et	Benzene	71	14	0.25

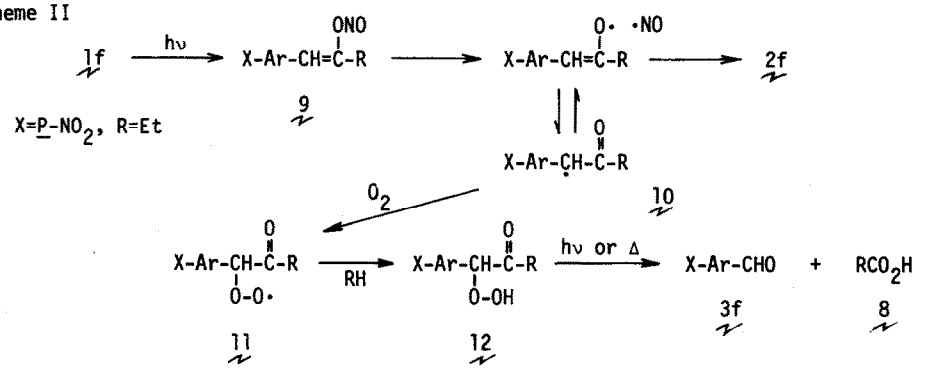
[a]Isolated yield. [b]Determined by nmr analysis of the reaction mixture.

On the other hand, irradiation of 1 in benzene under oxygen bubbling yielded substituted benzaldehyde 3 in almost quantitative yield. For example, irradiation of 1f in benzene under oxygen bubbling gave 3f (95 %) and propionic acid 8 (70 %). Under the conditions α-oximino ketone 2f yielded neither 3f nor 8. Under oxygen atmosphere, irradiation of 1d and methyl acrylate also yielded isoxazoline 7 (16 %). These results indicate that oxygen has no significant effect on the ratio of the two processes (path a and path b), and that a precursor for α-oximino ketone 2 is trapped by oxygen yielding 3f and 8.

The formation of 3f and 8 by the reaction of a precursor for 2f with oxygen may be rationalized by a mechanism involving a nitrite intermediate 9, which has been suggested to be an intermediate in the nitro to α-oximino ketone rearrangement.[2,4c] Thus, the nitrite 9 undergoes homolysis to give a radical species 10, which reacts with oxygen to yield 11. The

peroxy radical 11 or the α-keto hydroperoxide 12 may undergo thermal[12] or photochemical[13] cleavage reaction to yield 3f and 8. In the absence of oxygen the radical 10 combines with nitrogen oxide to give 2f (Scheme II).

Scheme II



In order to gain insight into the multiplicity of the reaction, we examined the quenching effect of piperylene on the formation of 2b and 3b in the photoreaction of 1b. Addition of piperylene inhibited the formation of 3b, but has no effect on the formation of 2b. The Stern-Volmer plots of the quenching reaction gave two straight lines (Fig. 1), indicating that there are two different excited states involving in the reaction. The excited state which is responsible for the formation of 3b (path b) is apparently the lowest triplet state, whereas the unquenchable state responsible for 2b may be a singlet state or a higher triplet state T_2, which still remains to be clarified. Irradiation of 1b in methanol with low pressure mercury lamp (Vycor filter, 253.7 nm) under nitrogen gave 2b (30 %), whereas irradiation of 1b under the conditions, where sufficient triphenylene (E_T=67 Kcal/mol, ϕ_{isc}=0.95[14]) was added to absorb >90 % of the incident light, gave 3b (17 %) but none of 2b.

Further studies are in progress on the mechanism of the photochemical reactions of nitro-olefins.

Acknowledgment. The authors are indebted to the Ministry of Education for a financial support.

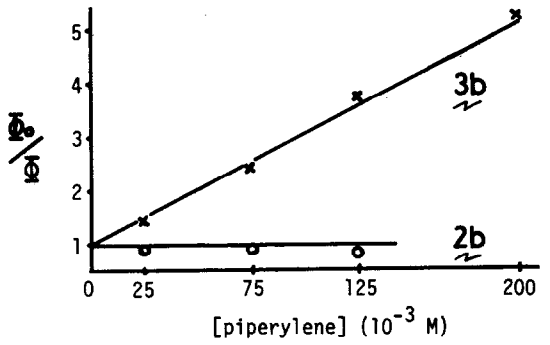


Fig. 1 Stern-Volmer plot for the piperylene quenching of the formation of 2b and 3b in the photoreaction of 1b in acetonitrile. [1b]=2.5 x 10^{-3} M.

REFERENCES AND NOTES

1. Photoinduced Reactions. LXXXIX.
2. O. L. Chapman, A. A. Griswold, E. Hoganson, G. Lenz, and J. Reasoner, Pure Appl. Chem., 9, 585 (1964).
3. a) O. L. Chapman, P. G. Clevland, and E. D. Hoganson, Chem. Commun., 110 (1966); b) J. T. Pinhey and E. Rizzardo, ibid., 362 (1965); c) J. S. Cridland and S. T. Reid, ibid., 125 (1969); d) R. Hunt, S. T. Reid, and K. T. Taylor, Tetrahedron Lett., 2861 (1972); e) G. B. Howarth, D. G. Lange, W. A. Szarek, and J. K. N. Jones, Can. J. Chem., 47, 81 (1969).
4. a) Y. Kitaura and T. Matsuura, Tetrahedron, 27, 1583 (1971); b) D. Döpp, Chem. Ber., 104, 1058 (1971); c) O. L. Chapman, D. C. Heckere, J. W. Reasoner, and S. P. Thackaberry, J. Am. Chem. Soc., 88, 5550 (1966); d) R. Hunt and S. T. Reid, J. Chem. Soc. Perkin I, 2527 (1972); e) M. B. Groen and E. Havinga, Mol. Photochem., 6, 9 (1974).
5. J. T. Pinhey and E. Rizzardo, Tetrahedron Lett., 4057 (1973).
6. a) I. Saito, M. Takami, T. Konoike, and T. Matsuura, Tetrahedron Lett., 2689 (1971); Bull. Chem. Soc. Japan, 40, 3805 (1973); b) I. Saito, M. Takami, and T. Matsuura, Tetrahedron Lett., 659 (1974); c) M. Takami, I. Saito, and T. Matsuura, ibid., 661 (1974); d) I. Saito, M. Takami, and T. Matsuura, Chem. Lett., 1195 (1972).
7. Satisfactory elemental analysis and the expected spectral data (ir, uv, ms, nmr) were obtained for all new compounds.
8. The compound was isolated as mixture of syn- and anti-isomer.
9. The nitrostyrene 1 undergoes rapid cis-trans photoisomerization, and the recovered 1 was isolated as mixture of cis- and trans-isomer.
10. In the case of 1d, the ratio 3d/2d was 0.31 for benzene, 0.29 for acetonitrile, and 0.28 for acetone.
11. a) M. Christl and R. Huisgen, Tetrahedron Lett., 5209 (1968); b) R. Huisgen and M. Christl, Angew. Chem., 79, 471 (1967); c) C. Grundmann, Synthesis, 344 (1970).
12. a) W. H. Richardson, V. F. Hodge, D. L. Stiggall, M. B. Yelvington, and F. C. Montgomery, J. Am. Chem. Soc., 96, 6652 (1974).
13. W. H. Richardson, G. Ranney, and F. C. Montgomery, ibid., 96, 4688 (1974).
14. N. J. Turro, "Molecular Photochemistry", p. 131, W. A. Benjamin, New York, N. Y., (1967).