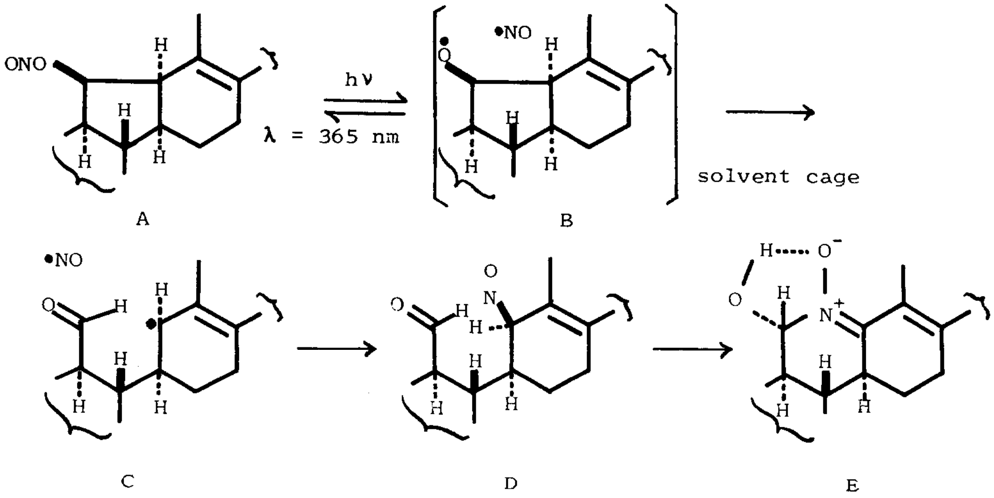
Tetrahedron Letters No. 49, pp 4723 - 4726, 1971. Pergamon Press. Printed in Great Britain

THE INTERMOLECULAR NATURE OF NITRIC OXIDE MIGRATION IN PHOTOCHEMICAL FORMATION OF CYCLIC NITRONES FROM NITRITES OF FUSED FIVE-MEMBERED RING ALCOHOLS (1)

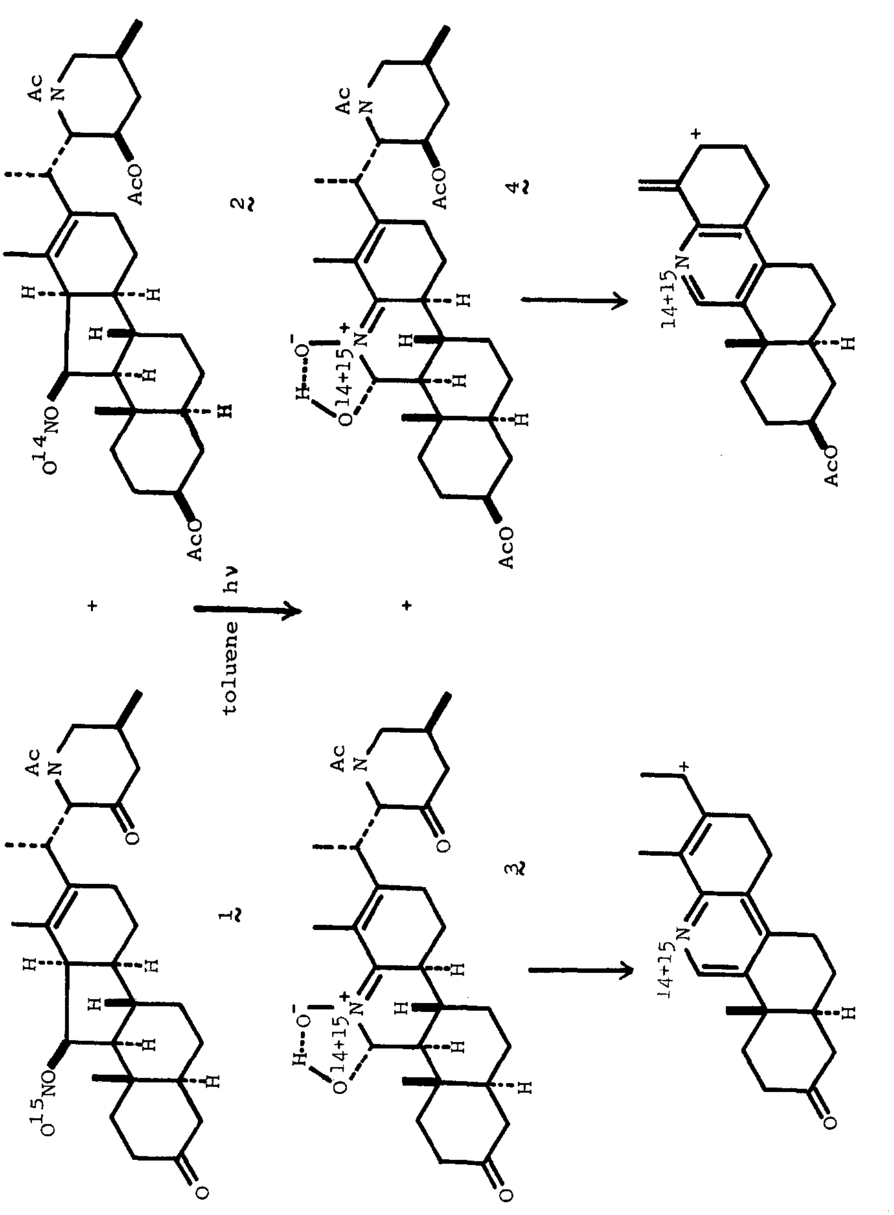
Hiroshi Suginome, Terutoshi Mizuguchi, and Tadashi Masamune,
Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo, Japan.

(Received in Japan 22 October 1971; received in UK for publication 2 November 1971)

In our previous papers, (2,3), we have shown that the excitation of the nitrites (partial structure A) of fused cyclopentanols in protic or aprotic media by 365 nm light induces stereospecific formation of cyclic nitrones (partial structure E). We have subsequently shown unambiguously that this cyclic nitrones are formed by the thermal cyclization of intermediary C-nitroso-aldehydes (type D) which are produced by the β-scission of alkoxyl radicals (type B) followed by the combination of NO and carbon radicals (type C), as shown in Scheme 1.



Scheme 1



5 m/e 308 (with ^{14}N)

6 m/e 324 (with ^{14}N)

Scheme 2

In this paper, we wish to report evidence which indicates the over-all migration of NO generated from the nitrito moiety into C-12 position of these molecules takes place in an intermolecular manner.

Thus, a new nitrite 1 (amorphous) labelled with ^{15}N (95.61 %) in its ONO group was prepared by the nitrosation of the corresponding C-nor-D-homosteroid-11β-ol (4). A mixture of this nitrite 1 (0.365 m moles) and nitrite 2 (0.365 m moles) with ^{14}N in its ONO group was photolyzed in toluene (18.2 ml) under an Argon atmosphere to afford two nitrones 3, m.p. 188-189° (18 %) and 4, m.p. 144-145° (41 %) (5).

Mass spectra of nitrones 3 and 4 with ordinary N showed their base peaks at m/e 308 (the isotope peak 309, 27.8 %) and at m/e 324 (the isotope peak 325, 25.6 %) assignable to the fragments 5 and 6. Then, the ratios of ^{15}N : ^{14}N in both nitrones obtained from the above photolysis were determined by mass spectrometric analysis, using fragment peaks due to 5 and 6 of the pure nitrones with ^{14}N for comparison. This showed that in nitrones 3 and 4, ratios of ^{15}N and ^{14}N were 1 : 2.3 and 1 : 2.7 respectively, proving that NO generated from the respective nitrites is randomly distributed in the product.

This result implies that in this nitrone formation, NO group present in the final product nitrone is not necessarily the NO group present in the parent nitrite.

In the initial reversible step in nitrite photolysis (Scheme 1), the formation of the nitrite from alkoxyl radical and NO has been proved to proceed via recombination of the original " geminate" pair (6). Therefore, the observed scrambling between ^{15}N and ^{14}N occurs only in the subsequent stages of the reaction.

Present results are parallel with the results obtained by Akhtar and Pechet for NO migration in the well-known Barton reaction (6). The observed lesser incorporation of ^{15}N into the both nitrones may be mainly due to the fact that the rate of decomposition of the nitrite 2 is faster than that of the nitrite 1.

REFERENCES AND FOOTNOTES

(1) Photoinduced Transformations. XIX. Previous paper in this series, H. Suginome, H. Takahashi, and T. Masamune, Bull. Chem. Soc. Japan, in press.

(2) H. Suginome, N. Sato, and T. Masamune, *Tetrahedron Letters*, 3353 (1969); *Tetrahedron*, in press.

(3) H. Suginome, T. Mizuguchi, and T. Masamune, *J. Amer. Chem. Soc.*, in press.

(4) This was prepared from jervine via 6 steps. Details of this preparation will be published in our full paper.

(5) Besides these nitrones, the presence of small amounts of unchanged two nitrites and the corresponding parent 11-ols in the product was observed on tlc.

(6) M. Akhtar and M. M. Pechet, *J. Amer. Chem. Soc.*, 86, 265 (1964).

ACKNOWLEDGEMENT

We are grateful to the staffs of the laboratory for mass spectrometric analysis of the Faculty of Pharmaceutical Sciences of this University for the mass spectral determinations.