Mechanism of Photochemical Formation of a Cyclic Nitrone from the Nitrite of a Fused Five-membered Ring Alcohol

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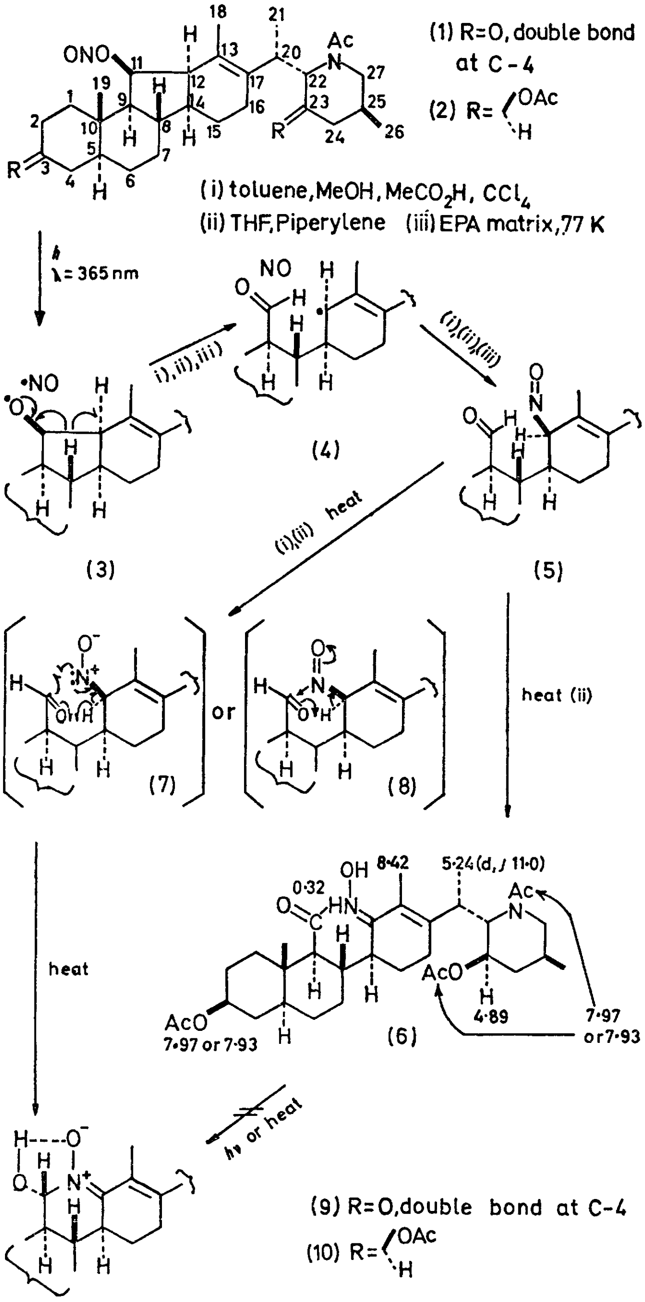
Summary On the basis of the results obtained from a monochromatic light experiment, the photolysis in EPA matrix at 77 K, and the photolysis in solvents such as CCl_4, it has been shown that the nitrone (**10**) is formed in a stereospecific manner by the thermal cyclization of a short-lived intermediate nitroso-aldehyde (**5**) from a fused cyclopentanol nitrite (**2**).



WE have recently reported that irradiation of a fused cyclopentanol nitrite (**1**) leads to the formation of a single novel cyclic nitrone (**9**).[1] We now report on an investigation which establishes the sequence involved in this reaction.

The nitrite (**2**), prepared from jervine, was photolysed in toluene or CCl_4 under the conditions described previously[1] to afford a single crystalline nitrone (**10**) (62 and 73%) as the only product (Scheme). When the nitrite (**2**) was photolysed in dry THF or piperylene, the major product (82 and 41%) was an oximino-aldehyde (**6**), (τ values given on the structure)† with a small amount of (**10**) (15 and 12%). The result obtained in piperylene suggests that the homolysis to the alkoxy-radical and NO occurs from an n, π^* singlet. (**10**) was formed even in acetic acid (61%). Both irradiation of (**6**) in toluene through Pyrex and thermal cyclization of (**6**) in toluene failed to give (**10**), in each case most of the starting (**6**) being recovered, thus ruling out the intervention of (**6**) as an intermediate. It follows, therefore, that the nitroso-aldehyde (**5**) is the immediate precursor for the cyclization and the following experiments unambiguously proved that (**10**) is formed by the thermal cyclization of a short-lived species (**5**).

Irradiation at 365 ± 7·5 nm of (**2**) in methanol, which excites the banded region of absorption due to n, π^* transition of (**2**), affords (**10**) ($\Phi = 0{\cdot}30$).‡ Since monochromatic light of 365 nm is unable to excite the formyl and the nitroso-group of (**5**), the remaining possibilities for the cyclization are either through excitation of these groups by an energy transfer from the excited nitrite or by thermal cyclization of (**5**).

The photolysis of (**2**) was undertaken in EPA matrix in two concentrations, 4×10^{-4} M and 7×10^{-2} M at 77 K through a Pyrex glass filter and the reaction was followed spectrophotometrically in the region 250—800 nm. It has been found that the two species absorbing at 693 and 323 nm are formed, and after about 3 min the latter reaches the maximum and then the species absorbing at 693 nm increases at the expense of the latter.§ The intensity and the position of the maximum of the former exactly corresponds to those due to n_N, π^* transition[2] of a *C*-nitroso-compound and an intermediary (**5**), which is too unstable to survive at room temperature, is assignable to this species.

The intensity of the absorption at 693 nm of the matrix remained unchanged after the maximum intensity was attained and no absorption at 284 nm due to nitrone appeared. This again excludes the involvement of excited

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† The i.r., u.v., and mass spectra were consistent with the assigned structure.

‡ A Jasco CRM-FA spectro-irradiator was used in these experiments. Quantum yield was determined with incident light of 365 nm and the formation of the nitrone was followed by u.v. spectroscopy. Light intensities were measured with Jasco Model RMI-I Light Integrator.

§ This has not been clarified but could be a charge-transfer band involving nitric oxide and an intermediate radical species.

(**5**) in the cyclization. After the matrix was brought to room temperature in the dark the examination of the solution revealed the formation of (**10**). This clearly shows that cyclization from (**5**) to (**10**) is a ground state reaction. The Scheme summarizes the steps involved in the reaction.

The formation of a single nitrone with the OH of α-configuration is explained by assuming that the original C-12 configuration of (**2**) is retained in the nitroso-aldehyde (**5**)[3] and the thermal cyclization may be achieved by a hydrogen transfer from C-12 to the newly formed carbonyl from the α-side of (**5**) through either a transition state (**7**) or a nucleophilic attack of the formyl carbon by the nitroso-group, *e.g.*, (**8**), to give (**10**).

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[1] For previous paper in the series "Photoinduced transformations", see H. Suginome, N. Sato, and T. Masamune, *Tetrahedron*, 1971, **27**, 4863.

[2] L. E. Orgel, *J. Chem. Soc.*, 1953, 1276; J. Mason, *ibid.*, 1957, 3904.

[3] C. H. Robinson, O. Gnoj, A. Mitchell, E. P. Oliveto, and D. H. R. Barton, *Tetrahedron*, 1965, **21**, 743; P. Kabasakalian and E. R. Townley, *J. Org. Chem.*, 1962, **27**, 3562.