A New Decomposition Route of Nitrate Esters

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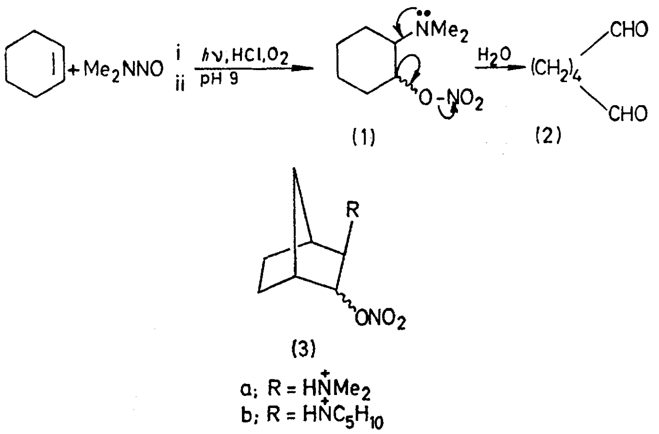
Summary Under basic conditions 2-aminocycloalkyl nitrate esters undergo amino-group-assisted cleavage of the C(1)–C(2) bond to give dialdehydes.

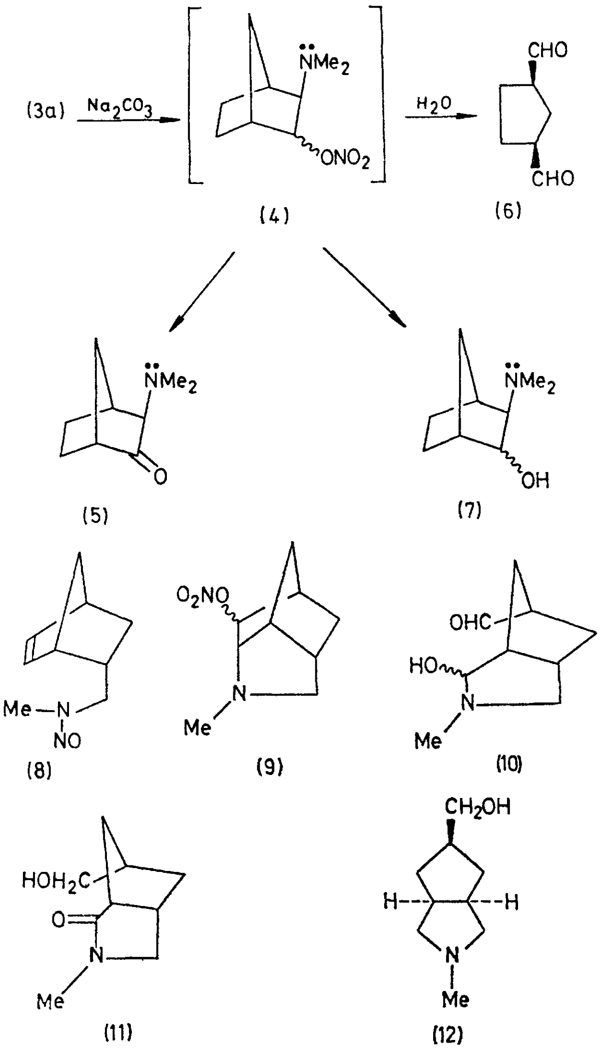
Photoaddition of *N*-nitrosopiperidine (NNP) or *N*-nitrosodimethylamine (NND) to cyclohexene under acidic conditions in the presence of oxygen yields a mixture of the hydrochlorides of *cis*- and *trans*-2-amino-nitrate esters.[1] The nitrate group is known to undergo C–O as well as O–N bond scissions.[2] In aqueous solutions, the nitrates (**1**) are stable at pH 1, but they gradually undergo solvolysis and elimination at pH 8—9 to form *cis*- and *trans*-2-aminocyclohexanols and 2-aminocyclohexanones.[1] A careful g.c.–m.s. analysis of the decomposition products shows that *ca.* 10% of dialdehyde (**2**) is also formed. Obviously the dialdehyde is derived from the cleavage of the C(1)–C(2) bond assisted by the lone-pair electrons of the amine group as shown in (**1**) (Scheme 1). This new mode of nitrate decomposition can become the major pathway depending on the structure of 2-amino-nitrate esters.



Scheme 1

Oxidative photoaddition of NNP to norbornene in the presence of perchloric acid and oxygen gave a mixture of the perchlorates of (**3b**) [*trans*, τ 4·58 (3-H, t, *J* 4 Hz); *cis*, τ 4·73 (3-H, d, *J* 7 Hz)] in about 1 : 1 ratio.† Similar oxidative photoaddition of NND to (**3a**) followed by basification gave a mixture (Scheme 2) which showed strong absorption at 1625, 1280, 870 cm^{-1} [for nitrate (**4**)], and 1720 cm^{-1} [for dialdehyde (**6**)] and a weak 1745 cm^{-1} shoulder [for ketone (**5**)] in which the nitrate peaks disappeared rapidly to give a more intense 1720 cm^{-1} peak on storage. Immediate reduction of the "basic" mixture with $LiAlH_4$ gave the amino-alcohols (**7**) [19%; *trans*, τ 6·51 (t, *J* 4 Hz), 7·80(s); *cis*, τ 6·56 (d, *J* 6 Hz), 7·72(s); ratio 3 : 7] from which *cis* (**7**) [i.r. (neat) 3300, 1050, 1035 cm^{-1}; τ 6·40 (1-H, dd, *J* 6·5 and 1·5 Hz), 7·62 (6-H, s)] was isolated by chromatography.

A decomposed "basic" crude product gave the bis-2,4-dinitrophenylhydrazone[3] of dialdehyde (**6**) (m.p. 224—225°, 71%) when treated with Brady's reagent and gave *cis*-1,3-bishydroxymethylcyclopentane[4] [isolated as the bis-*p*-nitrobenzoate (46%); m.p. 117—118°] when reduced with $LiAlH_4$. The decomposition of nitrates (**4**) into (**6**) is no doubt facilitated partially by a relief in the ring strain of the bicyclic ring system.



Scheme 2

The tendency to undergo cleavage was more striking in nitrate‡ (**9**), obtained from the intramolecular oxidative photoaddition of nitrosamine (**8**). The crude photoproduct underwent extensive decomposition on basification

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† N.m.r. spectra were taken in $CDCl_3$ solutions except that of the perchlorates of (**2**) which was taken in a $(CD_3)_2SO$ solution. The isolated compounds have satisfactory elemental analyses and spectroscopic data.

‡ On the basis of the reported propensity to cyclise to a five membered azacycles in intramolecular photoadditions of nitrosamines (ref. 5), we assumed that the nitrates (**9**), rather than the alternative 6-membered analogues, are formed. It should be mentioned that the initial cyclisation to the corresponding 6-membered analogues is also capable of giving pyrrolidine (**10**) and, therefore, (**11**) and (**12**) subsequently.

and resisted a chromatographic purification. Reduction of this crude mixture with $LiAlH_4$ gave the pyrrolidine (**12**) [36%; picrate m.p. 138—139°] which possessed a plane of symmetry as shown by a sharp doublet at τ 6·38 (J 5 Hz) for the CH_2O group. The complexity of the crude photoproducts is presumably not only due to extensive cleavage to give (**10**), but also to subsequent side reactions; for example, an intramolecular redox reaction of (**10**) (or its derivatives) to amide (**11**). Indeed further continuous extraction of the basified aqueous solution afforded amide (**11**) [9%; i.r. (neat) 3400, 1660 cm^{-1}] which was reduced by $LiAlH_4$ to (**12**).

Together with oxidative photoaddition of nitrosamines,[1] this cleavage reaction constitutes a one-step degradation of an olefinic bond as in ozonolysis and the decomposition of 2-nitrosoaminoalkane.[7] It is believed that the tendency toward cleavage is controlled by stereoelectronic factors such as antiperiplanar bond arrangement.[6]

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[1] Y. L. Chow, J. N. S. Tam, C. J. Colon, and K. S. Pillay, *Canad. J. Chem.*, 1973, **51**, 2469.
[2] P. A. S. Smith, 'Open-chain nitrogen compounds,' vol. II, W. A. Benjamin, New York, 1966, p. 484.
[3] R. H. Perry, Jr., *J. Org. Chem.*, 1959, **24**, 829.
[4] S. F. Birch and R. A. Dean, *J. Chem. Soc.*, 1953, 2477.
[5] Y. L. Chow, R. A. Perry, and B. C. Menon, *Tetrahedron Letters*, 1971, 1549.
[6] C. A. Grob, H. R. Kiefer, H. J. Lutz, and H. Wilkens, *Helv. Chim. Acta*, 1967, **50**, 416; P. S. Wharton and G. A. Hiegel, *J. Org. Chem.*, 1965, **30**, 3254.
[7] Y. L. Chow, C. J. Colon, and S. C. Chen, *J. Org., Chem.*, 1967, **32**, 2109.