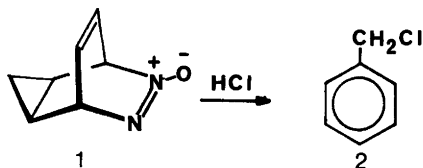


Acid Promoted Molecular Fragmentation of 6,7-Diazatricyclo-[3.2.2.0^{2,4}]nona-6,8-diene *N*-Oxide *

HENRIK OLSEN **

Department of General and Organic Chemistry,
The H.C. Ørsted Institute, University of
Copenhagen, Universitetsparken 5, DK-2100
Copenhagen, Denmark

Previously we have reported several reactions in which *cis*-1,2-diazene *N*-oxides undergo thermal and photolytically induced rearrangements.¹ In this communication we turn our attention to an acid catalyzed transformation in which 6,7-diazatricyclo[3.2.2.0^{2,4}]nona-6,8-diene *N*-oxide **1**² in the presence of hydrogen chloride undergoes fragmentation to yield benzyl chloride, nitrogen and water.³



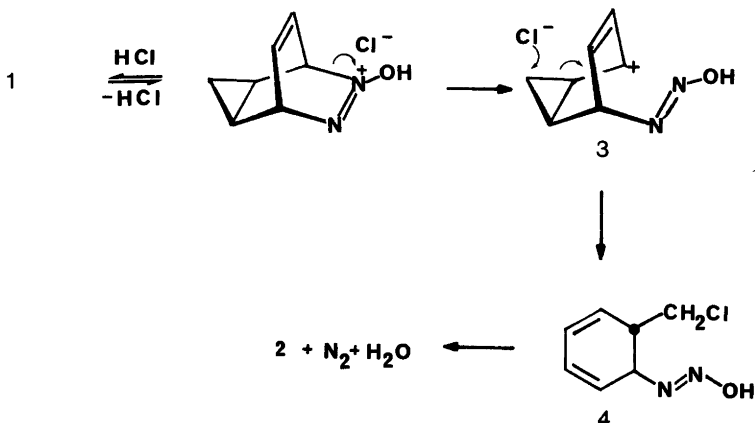
When **1** is mixed at room temperature with a solution of HCl in methanol (6 M), a vigorous reaction takes place with evolution of gas. The

* Rearrangement of 1,2-Diazene *N*-Oxides. 5. For Part 4, see Ref. 1.

** Present address: The Technological Institute, Gregersensvej, DK-2630 Tåstrup, Denmark.

¹H NMR spectrum of the crude reaction mixture (DCI, CD₃OD) was extremely simple, exhibiting only two singlets at δ 7.30 (5 H) and 4.60 (2 H), respectively, corresponding to benzyl chloride (80–85 % yield).***

The formation of benzyl chloride suggests that the reaction involves initial protonation at the *N*-oxide oxygen in **1**. Further transformation may proceed by heterolytic cleavage to give cation **3**. Collapse of **3** via cyclopropane ring-opening produces diazotic acid **4**. Finally, aromatization by extrusion of nitrogen and water accounts for the observed product. The depicted heterolytic cleavage is reminiscent of the behaviour of azoxy-2-methylpropane under the influence of trifluoroacetic acid⁴ and 3-chloro-3-phenyldiazirine in the presence of *m*-chloroperbenzoic acid.⁵ In contrast to the behaviour of **1**, 2,3-diazabicyclo[2.2.2]octa-2,6-diene *N*-oxide² is unchanged after analogous treatment with HCl for three months. Clearly the attachment of a cyclopropane ring significantly alters the energetics of the fragmentation reaction. This is in accordance with the well-documented unique stability of the cyclopropylcarbinyl cation.⁶ Since nitrous oxide was not detected in the reaction **1**→**2**, nitrogen is undoubtedly expelled during the aromatization depicted. The latter step is further supported by the work of Moss *et al.*⁷ on the solvolysis of alkanediazotates.



*** GLC-MS-analysis of the crude reaction mixture indicated the presence of minor amounts of methyl benzyl ether (2–5 %).

1. Olsen, H. *Helv. Chim. Acta* 65 (1982) 1921.
2. Olsen, H. and Snyder, J. P. *J. Am. Chem. Soc.* 99 (1977) 1524.
3. For other acid catalyzed rearrangements of 1,2-diazene *N*-oxides, see Hagerty, A. F. In Patai, S., Ed., *The Chemistry of the Hydrazo, Azo and Azoxy Groups*, Wiley, New York 1975, Vol. 1, Chapter 16, p. 711.
4. Greene, F. D. and Hecht, S. S. *J. Org. Chem.* 35 (1970) 2482.
5. Liu, M. T. H. and Li, J. C. W. *Tetrahedron Lett.* (1974) 1329.
6. Wilcox, C. F., Loew, L. M. and Hoffmann, R. *J. Am. Chem. Soc.* (1973) 8192 and references therein.
7. Moss, R. A. *Acc. Chem. Res.* 7 (1974) 421.

Received December 17, 1982.