Acid Promoted Molecular Fragmentation of 6,7-Diazatricyclo-[3.2.2.02,4]nona-6,8-diene N-Oxide *

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Previously we have reported several reactions in which cis-1,2-diazene N-oxides undergo thermal and photolytically induced rearrangements. In this communication we turn our attention to an acid catalyzed transformation in which 6,7-diazatricyclo[3.2.2.02,4]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.
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\[ \text{HCl (aq)} + \text{OH} \rightarrow \text{Cl}^- + \text{N-OH} \]

\[ \text{2 + N}_2\text{H}_2\text{O} \]

\[ \text{1} \]

\[ \text{2} \]

\[ \text{3} \]

\[ \text{4} \]

\[ \text{1} \text{H NMR spectrum of the crude reaction mixture (DCI, CD}_2\text{OD) was extremely simple, exhibiting only two singlets at 8 7.30 (5 H) and 4.60 (2 H), respectively, corresponding to benzyl chloride (80–85 % yield).} \]

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 acid 4 and 3-chloro-3-phenyl-diazirine 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-oxide 2 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 %).

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