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# MASS SPECTROMETRIC BEHAVIOR OF CIS-2,3-DIAZABICYCLO ALKANE DERIVATIVES AT DIFFERENTIAL OXIDATION LEVELS

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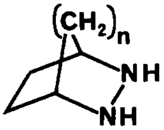
cis-2,3-Diazabicyclo [2·2·n] alkanes exist in four distinct oxidation states: dialkylhydrazine 1, azo alkane 2, azoxy alkane 3 and the diazoxy derivative 4.[1] Electron impact induced fragmentation within this series varies in an intriguing manner.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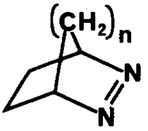
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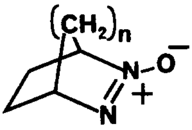
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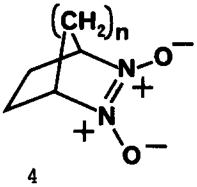
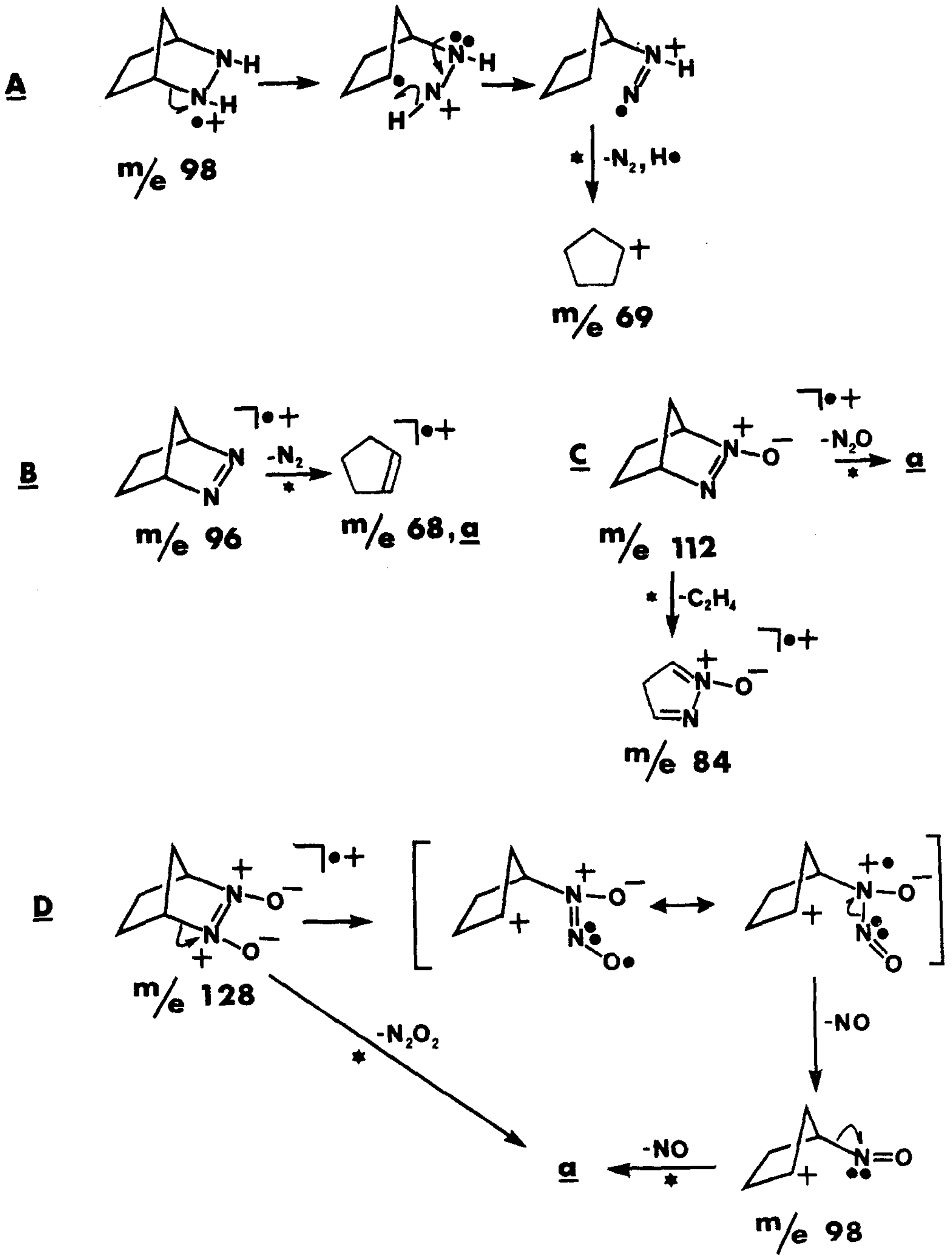

4

a;n=1
b;n=2

Hydrazine 1a,[2] introduced into the mass spectrometer as its hydrobromide salt, yields a parent ion at m/e 98 ($C_5H_{10}N_2$, 70% of base peak). The first major fragment at m/e 69 (100%) suggests internal hydrogen transfer followed by loss of the elements of $N_2H$ as depicted in Scheme A. This proposal is supported by the metastable peak at m/e 48.7. The remainder of the spectrum closely approximates that for cyclopentane[3]; loss of $N_2H_2$ is not observed.

The azo derivative 2a ($M^+$ $C_5H_8N_2$, m/e 96, 5%) decomposes (Scheme B) by an initial loss of 28 mass units. This is consistent with loss of

## Schemes A-D


A
m/e 98
-N₂, H•
m/e 69
B
m/e 96
-N₂
m/e 68, a
C
m/e 112
-N₂O
a
-C₂H₄
m/e 84
D
m/e 128
-N₂O₂
-NO
a
-NO
m/e 98

either ethylene or nitrogen. High resolution measurement of the resultant fragment m/e 68 (63%) demonstrates the presence of ion $C_5H_8$ (calc. m/e 68.0626; found 68.0627), possibly the radical cation a.[4] Nitrogen extrusion proceeds in parallel with thermal[5] and photochemical decomposition[6] of such systems. The corresponding azoxy derivative 3a, 2,3-diazabicyclo [2·2·1]-hept-2-ene-N-oxide,[7] likewise ejects a fragment of mass 28 (9%, Scheme C). High resolution measurement reveals ethylene to be that moiety (calc. $C_3H_4N_2O$ m/e 84.0324; found 84.0320). The primary fragmentation mode however, involves loss of $N_2O$ ($C_5H_8$, m/e 68, 100%) accompanied by the required metastable transition (m/e 41.2). Electron bombardment thus promotes both the expulsion of ethylene and $N_2O$ although the latter process is favored.[8]

The N,N'-dioxide, 4a,[9] ($M^+$ $C_5H_8N_2O_2$, m/e 128, 3%) eliminates its hetero atoms by sequential loss of NO ($C_5H_8NO$, m/e 98, 1%; $C_5H_8$, m/e 68, 25%). Scheme D suggests one possible fragmentation route. Initial cleavage of the parent ion to the dinitroso radical cation followed by stepwise loss of NO is likewise conceivable. Appearance of the appropriate metastable peak (m/e 36.2) for the transformation $C_5H_8N_2O_2 \rightarrow C_5H_8$ indicates that the $C_5H_8$ fragment arises likewise by direct loss from the parent ion.[10]

Fragmentation patterns below m/e 68 ($C_5H_8$) for 2a, 3a and 4a are essentially identical indicating a common hydrocarbon ion precursor.

A noteworthy aspect of the ion reactions described above, is the observation of significant ethylene loss from parent species corresponding to cis azoxy alkanes 3a and 3b. Mono-oxygenation of aliphatic cis-azo linkages is clearly attended by a reduced tendency of the molecule to expel its hetero elements. The thermal behavior of certain unsaturated aliphatic cis-azo-azoxy pairs mirrors this situation.[9] Both destruction modes suggest a considerably modified transition state for chelotropic fragmentation on passage from easily decomposed azo alkanes[11] to the corresponding N-oxides. The theoretical consequences of these observations shall be formulated in a forthcoming report.

Table

Major Mass Spectral Fragments of 1-4

| compound | m/e |
|---|---|
| 1a | 98,79,70,69[1],68,67,57,56,44,43,42,41. |
| 1b | 112,83,68,58,57,56[1],54,43,42,41,39. |
| 2a | 96,95,68[1],67,55,54,53,42,41,40,39. |
| 2b | 110,98,96,82,81,80,69,68,67,55,54,53,41[1]. |
| 3a | 112,84,82,68[1],67,66,55,54,53,42,41,40,39. |
| 3b | 126,110,98,96,82,81,80,69,68,67,55,54,53,41[1]. |
| 4a | 128,98,85,84,83,81,80,68,67[1],53,41,39. |
| 4b | 142,126,112,82,81,80,68,67[1],55,54,53,41,39. |

[1] base peak

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