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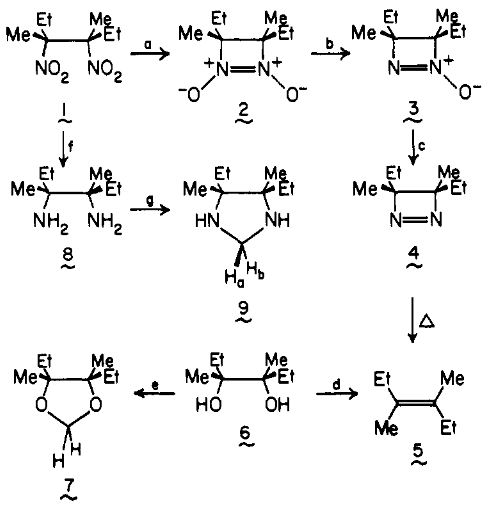
Decomposition of *meso*- and *dl*-3,4-Diethyl-3,4-dimethyldiazetine (a 1,2-Diaza-1-cyclobutene)[1]

Sir:

Study of the thermal decomposition of diazenes (azo compounds) has provided much information on the nature of diradicals and on the question of concerted vs. stepwise decomposition paths.[2] The four-membered-ring diazene—the 1,2-diazetine[3]—is of particular interest because of the variety of possible decomposition paths, and the relationships of these paths to orbital symmetry considerations and to questions associated with the high exothermicity in conversion of diazetines to olefins and N_2[3c] (e.g., the possibility of thermal generation of electronically excited states).[4] We report here the synthesis and stereochemistry of decomposition of *meso*- and *dl*-3,4-diethyl-3,4-dimethyldiazetine (*meso*-**4** and *dl*-**4**). The principal finding is that loss of N_2 from *meso*-**4** and *dl*-**4** is stereospecific and cis, affording *cis*- and *trans*-3,4-dimethyl-3-hexene, respectively.

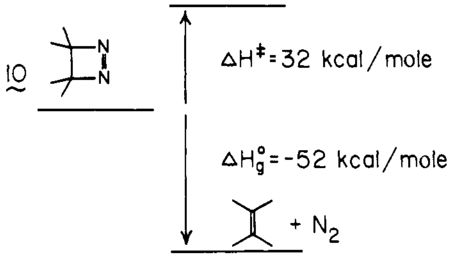
Synthesis of diazetines **4** (shown in Scheme I for the *dl* series): samples of **4** enriched in the meso or *dl* isomer were obtained by fractional recrystallization of *meso*- and *dl*-3,4-dimethyl-3,4-dinitrohexane (**1**),[5] followed by the sequence **1** → **2** → **3** → **4**. Assignments of stereochemistry (Scheme I): the meso and *dl* designations for diazetines **4** are based on conversion of dinitrohexane **1** to diamine **8** to imidazolidine **9**; NMR data of the ring methylene protons of imidazolidine **9** are definitive for stereochemical assignment (*meso*-**9** shows an AB quartet at δ 3.79, *dl*-**9** a singlet at δ 3.85). Assignment of olefin **5** stereochemistry is based on conversion of diol **6** to dioxolane **7** and to olefin **5**. In dioxolane **7**, the ring methylene protons appear as an AB quartet at δ 4.96 in the meso isomer and as a singlet at δ 4.98 in the *dl* isomer. The *dl*-dioxolane **7** was derived from the crystalline diol of mp 52-53 °C, thereby rigorously established as the *dl*-diol.[6] This same diol has been converted[7] by the cyclic thionocarbonate-triethyl phosphite reaction (known to involve overall cis elimination of the hydroxyl groups)[8] to one of the isomers of 3,4-dimethyl-3-hexene, established from the above relationships as the trans isomer.[9]

Scheme I[a]



[a] (a) (1) Zn, NH_4Cl, (2) Br_2; (b) Si_2Cl_6, CH_2Cl_2; (c) $LiAlH_4$; (d) (1) RLi, CS_2, CH_3I, (2) Et_3P; (e) CH_2O; (f) Sn, HCl; (g) CH_2O.

Scheme II



Pyrolysis of samples of diazetine **4**, enriched in meso and *dl*, at 375 °C (GC injection point) gave the isomeric hexenes **5** (eq 1 and 2). Within the limits of these experiments,[10] the decompositions are stereospecific and involve cis elimination of N_2.

diazetine **4** → 3,4-dimethyl-3-hexene (**5**)

$$>95\%\ meso\text{-}\mathbf{4} \rightarrow >95\%\ cis\text{-}\mathbf{5} \tag{1}$$

$$58 \pm 2\%\ dl\text{-}\mathbf{4} \rightarrow 56 \pm 2\%\ trans\text{-}\mathbf{5} \tag{2}$$

The enthalpy changes associated with the decomposition of 3,3,4,4,-tetramethyldiazetine (**10**)[3b,c] to tetramethylethylene are summarized in Scheme II.[11] The energy liberated in going from the transition state of diazetine **10** decomposition to ground state of products is ~85 kcal/mol, substantially above the amount associated with the interconversion of cis and trans olefins. In spite of this, the thermal decomposition of *meso*- and *dl*-diazetine **4** proceeds with high stereospecificity. The high stereospecificity also indicates that crossover to the T_1 state of 3,4-dimethyl-3-hexene (**5**) has not taken place;[12,13] the S_1 state of **5**, lying more than 130[13c] kcal/mol above S_0, would be energetically inaccessible in this reaction.

It is also of interest to consider the implications of the stereochemical findings with regard to synchronous vs. stepwise decomposition of diazetines. Evidence favors the loss of nitrogen from cyclic azoalkanes by concerted two-bond cleavage.[3c] Engel has suggested that the sum of the ground-state strain energy and $\Delta H^{\ddagger}$ for thermolysis is approximately constant at 42-45 kcal mol^{-1} for monocyclic azoalkanes.[3c,14] For diazetine **10**, this sum is 56 kcal mol^{-1}, indicating that **10** decomposes with at least 11 kcal mol^{-1} more difficulty than the five- and six-membered-ring counterparts.[3c] This finding is in accord with orbital symmetry restrictions on a $[2_s\ (\text{olefin}) + 2_s\ (N_2)]$ process in the four-membered-ring case.[3a] The cis elimination of N_2 from *meso*- and *dl*-**4** excludes the orbital symmetry allowed possibility of synchronous loss of N_2 by a $[2_a\ (\text{olefin}) + 2_s\ (N_2)]$ path. The synchronous alternatives of $[2_s\ (\text{olefin}) + 2_a\ (N_2)]$ or of $[2_s\ (\text{olefin}) + \text{"partial } 2_a\text{"}\ (N_2)]$[15] remain.

Concerning possibilities for stepwise decomposition of diazetine **4** (shown in Scheme III), the finding of cis elimination of N_2 leads to two conclusions: (a) cleavage of a C-N bond in **4** does *not* occur via concomitant stretching and twisting to diradical A, since this species would inevitably afford both *cis*- and *trans*-hexenes **5**; (b) if cleavage occurs by C-N stretching to afford diradical B, then the rate of loss of N_2 from this diradical (k_{frag}) exceeds the rate of rotation around the central C-C bond (k_{rot}). Prediction of the relative magnitudes of k_{frag} and k_{rot}, both expected to be of low activation energy, is rather speculative; analysis of ESR data on bond rotations in radicals,[16] of the results of decomposition of an optically active diazene,[17] and of CIDNP data[18] leads us to conclude that for

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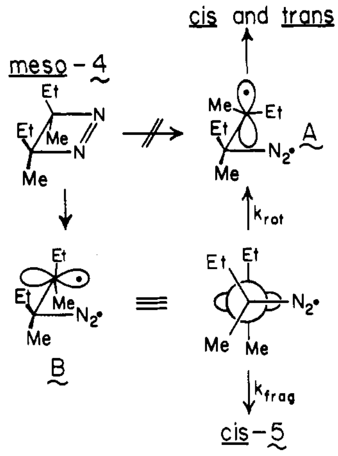
Scheme III



diradical B k_{frag} may well exceed k_{rot}; i.e., the observation of overall cis elimination of N_2 from diazetine **4** does not exclude a stepwise decomposition mechanism for diazetines, e.g., via diradical B.[19]

In summary, these results (a) indicate the unimportance of electronically excited states in this highly exothermic reaction, (b) exclude one of the most probable of the possible synchronous modes of decomposition, (c) place severe constraints on the nature of the lifetime of a diradical derivable by a stepwise mode of decomposition.

References and Notes

(1) Supported, in part, by the National Science Foundation and the National Institutes of Health.

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(4) (a) See G. B. Schuster, N. J. Turro, H.-C. Steinmetzer, A. P. Schaap, G. Faler, W. Adam, and J. C. Liu, *J. Am. Chem. Soc.*, **97**, 7110 (1975), and references therein; K. A. Zaklika, P. A. Burns, and A. P. Schaap, *ibid.*, **100**, 318 (1978). (b) See also C. R. Jones and P. B. Dervan, *ibid.*, **99**, 6772 (1977).

(5) Satisfactory combustion and spectral data were obtained for the new compounds in this study. Analysis of the isomer composition of dinitrohexane **1** was made by GC on a 15% SE-30, Chromosorb W column. The *meso*-**1** (chunky rosettes) has mp 87–88 °C; *dl*-**1** (plates) mp 85–86 °C. Separation of the isomers of diazetine *N*-oxide (**3**) or diazetine **4** could not be effected under a variety of GC conditions examined. Compounds **1**, **2**, **3**, **4**, and **8** all showed some differences in the ^1H NMR for meso and *dl* forms, from which it was clear (as expected) that all of these interconversions occurred without loss of stereochemical integrity.

(6) This compound has been considered to be the *meso*-diol: W. Reeve and M. Karickhoff, *J. Am. Chem. Soc.*, **78**, 6053 (1956).

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(8) E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963).

(9) Relative retention times on 25% dimethylsulfolane on Chromosorb P: octane (1.0), *trans*-**5** (1.50), *cis*-**5** (1.63). Other evidence in support of these olefin assignments: J.-G. Duboudin and B. Jousseaume, *J. Organomet. Chem.*, **44**, C1 (1972); Dr. Greenlee of Chemical Samples Co., acetate pyrolysis data (private communication to F. D. Greene).

(10) The limits of analysis were set by the proximity of the NMR peaks in *meso*- and *dl*-**4** and by the (small) overlap of the peaks for cis and trans olefins **5** in the GC trace.

(11) $\Delta H°_g = \Delta H°_l$ (tetramethylethylene) $- \Delta H°_f$ (**10**) $= -16.4 - 35.9^{3c} = -52.3$ kcal/mol.

(12) (a) The T_1 state is expected to lie <75 kcal/mol above the S_0 state of the hexene **5** (e.g., see S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973). (b) The branching ratio for triplet 2-butene is 1.02; see E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *J. Chem. Phys.*, **48**, 4547 (1968). (c) Based on lack of absorption at wavelengths >210 nm (see also G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1966, p 533).

(13) Crossing to a T_1 state of a product does appear to take place in the thermal decomposition of dioxetanes.[4a]

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(15) A 2_a (N_2) would involve 180° rotation about the N–N bond in the process of decomposition of **4**; "partial 2_a" (N_2) would involve 90° rotation about the N–N bond.

(16) See H. Fischer in "Free Radicals", Vol. 2, J. K. Kochi, Ed., Wiley, New York, 1973, p 482–483 and references cited.

(17) A. Tsolis, S. G. Mylonakis, M. T. Nieh, and S. Seltzer, *J. Am. Chem. Soc.*, **94**, 829 (1972).

(18) N. A. Porter, G. R. Dubay, and J. G. Green, *J. Am. Chem. Soc.*, **100**, 920 (1978). See also A. R. Lepley and G. L. Closs, "Chemically Induced Magnetic Polarization", Wiley, New York, 1973, p 112–117.

(19) Of interest is the comparison of the predominance of cis elimination of N_2 in this study with the low selectivity observed in some cyclic peroxide, six-membered-ring disecondary systems;[4b] see also P. B. Dervan and T. Uyehara, *J. Am. Chem. Soc.*, **98**, 1262 (1976).

(20) American Association of University Women Fellow, 1975–1976.

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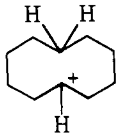
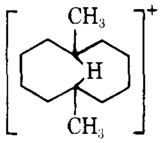
The Observable Cyclodecyl Cation. A Novel "Secondary" Hydrogen-Bridged Carbocation

Sir:

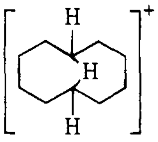
The cyclodecyl cation (conventionally written as **1**), a well-studied[1] reactive intermediate noted for its ability to undergo transannular hydride shifts, has now been prepared and characterized in strong acid solution and we describe herein the very unusual features of both the ^1H and ^{13}C NMR spectra which lead us to conclude that this cation, like the previously described 1,6-dimethyl analogue **2**,[2] possesses a 1,6-μ-hydrido structure **3**.



1



2



3

Addition of 1-chlorocyclodecane to a solution of either 1:1 SbF_5–FSO_3H or pure SbF_5 in a mixture of SO_2ClF–SO_2F_2 at ca. −140 °C or the addition of either *cis*- or *trans*-cyclodecene to the 1:1 SbF_5–FSO_3H mixture[3] results in a light yellow solution showing similar NMR features.[4] The proton spectrum measured at −130 °C[5] is the most informative and is characterized in particular by two broad peaks,[6] one at δ 6.80 and a second of one half the area at δ −6.85, a unique high-field position range shown previously[2] to be characteristic of the bridging hydrogen in **2**. These two peaks can therefore be assigned to the terminal and bridging hydrogens of a μ-hydrido structure, i.e., partial structure **4**. Coupling, if any, between these protons is obscured by the broadness of the peaks.[7] The remaining 16 protons in **3** form a broad envelope of overlapping peaks from ca. δ 1–3.[8]

The lowest field ^{13}C peak (−130 °C) is found at δ 152.8[9] and is assignable to the two carbons involved in the hydrido bridge. Careful selective ^1H decoupling experiments[10] show that this ^1H coupled ^{13}C peak is a doublet of doublets with remarkably different coupling constants, $J_{^{13}C-^1H} = 158 \pm 5$ and 32 ± 5 Hz, the former from coupling to the δ 6.8 ^1H peak and the latter the coupling of this carbon to the high-field "μ-hydrido" proton.[11] The completed NMR characterization of the bridged region in **3** can be compared with the corresponding parameters in diborane, cf. **4** vs. **5**.[11]

Quenching experiments have been carried out on the cyclodecyl cation by adding the cation solution to vigorously

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