

Table I. Heat of Reaction for Deazoxetation of Some Unsaturated Azo *N*-Oxides

Compd	No. of runs	T_i , °K	Solvent	$-\Delta H_{\text{react}}$, ^b kcal/mol
4	6	452	THF- <i>d</i> ₈	0.84 ± 0.06
5	3	446	THF- <i>d</i> ₈	0.71 ± 0.12
6	4	426	THF- <i>d</i> ₈	2.31 ± 0.09
7	5	413	THF- <i>d</i> ₈	9.85 ± 0.13
	5	422	CD ₃ CN	9.34 ± 0.23
8	4	337	THF- <i>d</i> ₈	16.38 ± 0.85
	4	341	CD ₃ CN	14.99 ± 0.34

^a Temperature at which the maximum heat flux due to the reactions is observed. ^b All errors are reported as ± 5; see J. D. Cox and G. Pilcher "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y. 1970, pp 43, 44.

N-oxides. By combination of these quantities with thermochemical group increments and reasonable strain energies, it is possible to arrive at an approximate heat of formation for the azo *N*-oxide group: ΔH°_f (*cis*-azo *N*-oxide) = 35–40 kcal/mol.²⁷ In view of the recently established ΔH°_f for the *cis*-azo group (54 kcal/mol),¹⁴ oxidation of the azo to the azoxy moiety is clearly a highly exothermic process (15–20 kcal/mol).²⁸ The resulting thermochemical stabilization is in accord with the formation of a new σ bond, π -electron delocalization over the three heteroatoms, and the elimination of the azo α lone-pair repulsion.

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References and Notes

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- ΔE_g and $k_{\text{azo}}/k_{\text{azoxy}}$ have been recalculated⁴ assuming a $\Delta S^\ddagger = +5.0$ eu.
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- A full description of the calorimeter and data analysis will be published elsewhere; cf. J. F. M. Oth, *Recl. Trav. Chim. Pays-Bas*, **87**, 1185 (1968).
- Prepared by a route analogous to the other unsaturated azo *N*-oxides.^{1,4} Compound **5** exhibits consistent spectroscopic properties and yields a satisfactory elemental analysis.
- For each run the sealed Pyrex ampules were monitored after thermolysis by ¹³C and ¹H NMR. With the exception of **4** and **5** the only observable product was the diene corresponding to retrocycloaddition. For the former, in addition to the primary products, benzene (for **4**) and dimers (for **4** and **5**) were detected.
- We are grateful to P. Engel (Rice University) for suggesting this method for arriving at ΔH°_f (**3**).
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- The diminutive value of correction i is substantiated by the data in Table I. Factor ii is small since, although C_p° (gas) values for individual species may be large, ΔC_p° (gas) for reactions is considerably less and consequently responds insignificantly to changes in temperature (cf. ref 13a, pp 20, 32). We calculate 0.5–1.7 kcal/mol. With regard to correction iii, it should be pointed out that N₂O is most likely in the gas phase during the calorimetric measurements since its critical temperature is T_c 36.5 °C and its critical pressure is $P_c = 74.1$ atm. Assuming nonideal gas behavior, application of either the principle of corresponding states^{16a} or the virial equation with maintenance of the second virial coefficient^{16b} leads to a pressure correction of 0.08 kcal/mol.

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- (17) The heat of vaporization of 2,3-diazabicyclo[2.2.1]hept-2-ene and 2,3-diaza-1,4-dimethylbicyclo[2.2.2]oct-2-ene have been determined to be 13.2 and 17.2 kcal/mol, respectively.¹¹ The difference in dipole moment between 2,3-diazabicyclo[2.2.2]oct-2-ene and the corresponding *N*-oxide is 1.6 D.¹⁸ Consequently a ΔH_v (**4**) = 20 ± 4 kcal/mol is assumed.
- (18) Dr. C. Larsen, University of Copenhagen, unpublished results.
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- (26) J. P. Snyder, L. Lee, V. T. Bandurco, C. Y. Yu, and R. J. Boyd, *J. Am. Chem. Soc.*, **94**, 3260 (1972).
- (27) In accord with the procedure indicated for the calculation of ΔH°_f (**3**, g, 298 K), the quantities ΔH (298 K, g), ΔH°_f (cyclic dienes) and ΔH°_f (N₂O) were combined to give an average value for ΔH°_f (*cis*-azo *N*-oxide).
- (28) Although the oxidation of amines and pyridines to the corresponding *N*-oxides is generally acknowledged to be an exothermic process, to our knowledge this is the first quantitative estimate of the energy gain.

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Generation and Capture of Common Intermediates from Proto-Planar and Proto-Bisected Trimethylenemethane Precursors. Thermal Rearrangement of a Methylene-pyrazoline¹

Sir:

Theory suggests² that the stable forms of triplet and singlet trimethylenemethanes (TMMs) should be, respectively, planar and bisected. We now report the results of an attempt to generate a planar and a bisected TMM independently by decomposition of the isomeric methylenepyrzazolines **1** and **2**. The "proto-planar" bridged compound **1** could be imagined to lose molecular nitrogen thermally and give a planar singlet without any torsion about the bond joining the exocyclic Me₂C group to the five-membered ring, whereas the "proto-bisected" fused compound **2**, by a similar process and rehybridization of that group, would give a bisected TMM. If these TMM species have separate existences as long as 10⁻⁹ s, it might be possible to capture them with external reagents and observe different products from each.

For such a study to be interpretable, it is necessary to show that the methylenepyrzazolines **1** and **2** have separable pathways of deazetation. Without this information, common

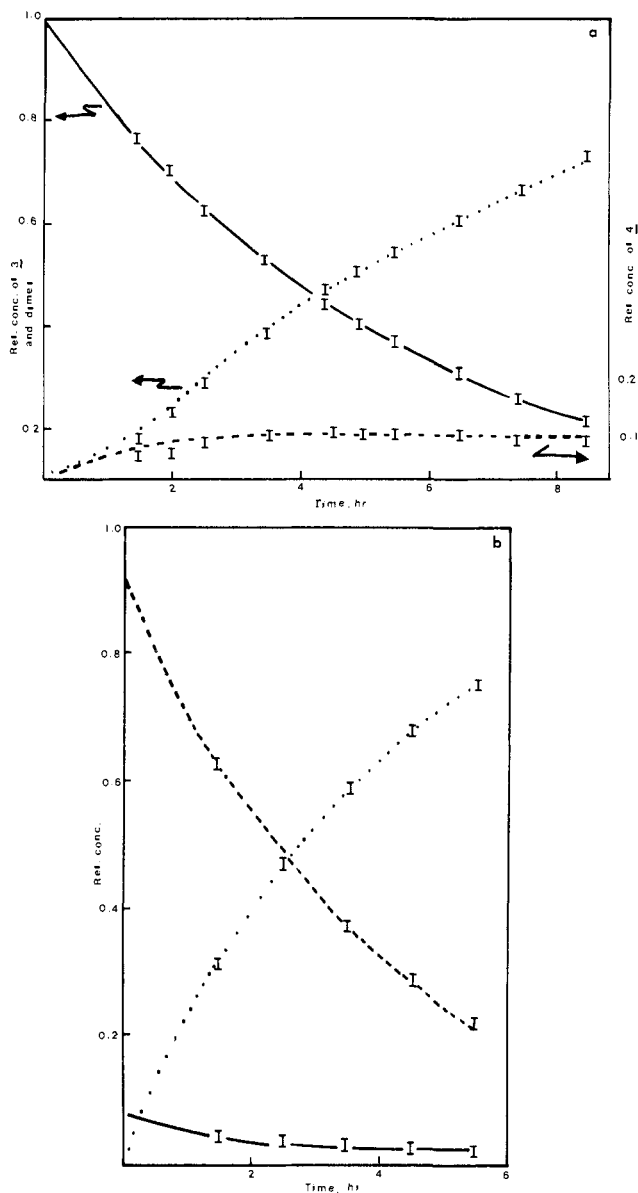
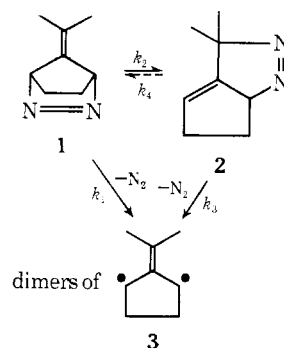


Figure 1. Relative concentration of diazenes and product dimers as a function of time during the pyrolysis of **1** (a) and **2** (b) in CH_3CN solution at 50.0°C . The experimental points and their estimated uncertainties are shown. The solid, dashed, and dotted curves show the behavior predicted for **1**, **2**, and dimers, respectively, by numerical integration of the differential equations of Scheme I using the rate constants given in the text. The "dimer" concentrations shown represent the amount of deazetation. Actual dimer concentrations are half of these values.

products could signify either common intermediates or a fast rearrangement, which could equilibrate **1** and **2** prior to decomposition. Although previous careful searches³ showed the absence of such rearrangements in simple TMM precursors, there are scattered observations of allylic rearrangement of the starting material during decomposition of other acyclic⁴ and cyclic^{5,6} diazenes. We now find that deazetation without rearrangement is not general for methylenepyrzoline TMM precursors, because isomerization to the fused diazene **2** accompanies the thermal decomposition of the bridged isomer **1** (Scheme I).

The detection of the **1** \rightarrow **2** rearrangement is difficult by ordinary NMR spectroscopy, because of the close chemical shift correspondence of the characteristic peaks. However, in CDCl_3 solutions, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium ($\text{Eu}(\text{Fod})_3$), which is known⁷ to complex with *cis*-diazenes, produces different

Scheme I



pseudocontact shifts for the methyl signals of **1** and for the nonequivalent methyl signals of **2** and thereby permits quantitative analysis of the chromatographically recovered (Florisil, pentane, and then Et_2O) diazenes from partial pyrolyses. Figures 1a and 1b show the relative concentrations of **1**, **2**, and product dimers as functions of time in thermal decompositions at 50.0°C in CH_3CN solution. The reactions start with pure **1**⁸ and with an enriched sample of **2**^{9a} (92.8% **2**, 7.2% **1**), respectively.

The kinetic behavior can be fitted to the triangular mechanism of Scheme I with rate constants determined by a computer-assisted Runge-Kutta numerical integration¹⁰ of the differential equations. The set of rate constants ($\times 10^5 \text{ s}^{-1}$) $k_1 = 3.50$, $k_2 = 1.50$, $k_3 = 7.35$, and $k_4 = 0$ fit the relative concentrations of **1**, **2**, and products (dimers of the biradical **3**) with root mean square errors of 0.023, 0.029, and 0.031 from the pyrolysis of **1** (Figure 1a) and 0.009, 0.009, and 0.001 from the pyrolysis of **2** (Figure 1b).

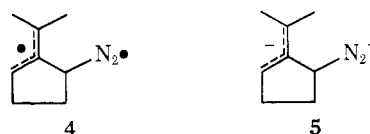
In Scheme I, if $k_4 = 0$, the disappearance of diazene in the pyrolysis of **2** would be simply a first-order reaction with rate constant k_3 . Experimentally, this reaction obeys first-order kinetics with a rate constant $(7.34 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$, which agrees exactly with the computer-fitted value of k_3 . Moreover, the integrated form¹¹ of the Scheme I kinetics when $k_4 = 0$ gives

$$-\ln(1/1_0) = (k_1 + k_2)t \quad (1)$$

which predicts that the disappearance of **1** also should be first order. This is again in agreement with experiment, the rate constant $4.96 \times 10^{-5} \text{ s}^{-1}$ being very close to the sum $k_1 + k_2 = 5.00 \times 10^{-5} \text{ s}^{-1}$ determined by numerical integration. A good fit to the data of Figure 1a also can be obtained assuming a reversible **1** \rightleftharpoons **2** interconversion, with k_1 , k_2 , and k_3 having about the same values as before and $k_4 = 3.0 \times 10^{-6} \text{ s}^{-1}$, approximately 20% k_2 . However, the fit to Figure 1b is decidedly worse than when $k_4 = 0$. Evidently, the **1** \rightarrow **2** reaction is essentially irreversible under these conditions. If we accept the ratio $k_4/k_2 \leq 0.2$ implied by the kinetic analysis, the bridged diazene **1** is less stable than the fused isomer **2** by $\Delta G^\circ \geq 1.04 \text{ kcal/mol}$.

The formal 1,3-sigmatropic thermal rearrangement **1** \rightarrow **2** in principle might occur intramolecularly or by recapture of molecular nitrogen by the biradical **3**. The absence of **1** \rightarrow **2** rearrangement when the same^{12,13} biradical is generated photochemically favors an intramolecular interpretation of the thermal process.¹⁴

A plausible mechanism would involve the diazenyl biradical **4** or its zwitterionic relative **5**. We have previously reported¹³



that the rates and activation parameters for the thermal deazetation of **1** in the solvents CH₃CN and benzene are identical. This suggests that, if the rate-determining steps of the rearrangement and deazetation both pass over the same intermediate, the biradical **4** is the preferred formulation.¹⁵

The portion of bridged diazene **1** proceeding directly to trappable reactive intermediates and not funneled through fused diazene **2** is given by $100[k_1/(k_1 + k_2)] = 70\%$. Thus, despite the competing rearrangement, most of the **1** and essentially all of the **2** decompose separately.

Bridged diazene **1** can be recovered from 15 runs representing increasing extents of partial photolysis (7–99% reaction, CH₃CN solution, 0 °C, 350 nm), but no rearrangement (<5%) to the fused isomer can be detected. This is in agreement with the quantum yield of 0.95 ± 0.05 for the photo-deazetation of **1**.¹² Here also, the deazetations are effectively independent.

Comparisons of the composition of the cycloadduct mixture obtained by thermal or photochemical decompositions of diazene in the presence of an efficient singlet trapping agent (dimethyl fumarate or fumaronitrile)^{9b,c} shows the products from **1** and **2** to be identical. Any distinction in structure between the singlet intermediates from proto-planar and proto-bisected precursors either fortuitously fails to result in distinctive reactivities, or, more plausibly, is lost during the lifetime of the intermediate. It is possible that the product equivalences observed here could be attributable to the common intermediacy of the diazenyl biradical **4**. Conceivably, a different method of generating the TMM **3** could still demonstrate independent identities for the planar and bisected forms.

The previously reported¹² low-temperature flash photolysis technique facilitates a further search for intermediates, including the bisected triplet, which might intervene between the proto-bisected diazene **2** and the planar triplet. A sample of **2** in solution is frozen to 4.2 K in the cavity of the ESR spectrometer and exposed to a xenon lamp flash. The ESR signal, monitored at the strong (inside) line of the $\Delta m = 1$ transition with a time resolution of $\sim 5 \times 10^{-2}$ s, rises sharply and without delay to a stable level. A more leisurely scan of the spectrum so generated shows it to be identical with that observed^{8,16} upon photolysis of the proto-planar diazene **1**. If ESR-inactive intermediates had been generated from **2**, survived longer than 5×10^{-2} s, and then decayed to the planar triplet, the flash-induced signal either would have passed through a maximum or would have shown a delayed gradual rise.

From the average lifetime of $< 5 \times 10^{-2}$ s at 4.2 K in the photodeazetation of proto-bisected diazene **4**, we may conclude that any ESR-inactive intermediates encounter no significant (<190 cal/mol) activation barrier in the pathway leading to the observed triplet. Furthermore, if the bisected triplet lies on this pathway, either its ESR spectrum is very similar to that of the planar triplet,¹⁷ or it is a species of only fleeting existence.

References and Notes

- (1) The support of this work by grants from the National Science Foundation (GP-33909X and CHE-76-00416) and from the National Institute of General Medical Sciences (GM-23375) is gratefully acknowledged.
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- (10) The computer program, kindly provided by Professor Martin Saunders, was modified slightly for use with the PDP-1145 system by Dr. Barry K. Carpenter.
- (11) Cf. R. A. Alberty and W. G. Miller, *J. Chem. Phys.*, **26**, 1231 (1957).
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- (14) We are indebted to Professor J. M. McBride for this insight and for calling our attention to the work cited in ref. 6.
- (15) Activation parameters for the thermal first-order deazetation of fused diazene **2** in CH₃CN solution are $\log A = 14.9$ (A in s^{-1}), $E_a = 28.0$ kcal/mol, as compared to values of 15.1 and 28.8 for **1**.¹³ The last two entries of Table I in ref. 13 should read 28.8° and 27.6°. The $\log A$ and E_a values reported¹³ for **1** are not corrected for the 30% of the deazetation that takes place via **2**. We assume that the deazetation and rearrangement E_a values do not differ greatly.
- (16) M. S. Platz, J. M. McBride, R. D. Little, J. J. Harrison, A. Shaw, S. E. Potter, and J. A. Berson, *J. Am. Chem. Soc.*, **98**, 5725 (1976).
- (17) Mr. M. W. Vary has pointed out that the values of the zero field splitting parameter D for the planar and bisected forms of TMM, calculated from the simple Hückel spin density distributions, do not differ greatly. Hence, the planar and bisected species might have rather similar ESR spectra.

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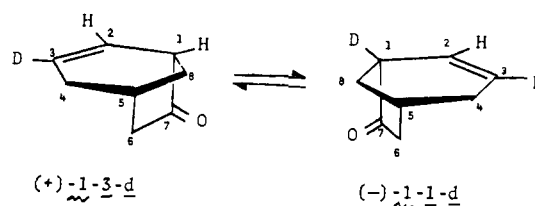
A Thermal [1,3] Sigmatropic Acyl Shift in the Degenerate Rearrangement of Bicyclo[3.2.1]oct-2-en-7-one

Sir:

Thermal [1,3] shifts of acyl or carboalkoxy groups are rare and perhaps unprecedented.¹⁻⁶ The difficulty of such reactions might be rationalized plausibly on the grounds that steric factors favor suprafacial migration, and therefore orbital symmetry^{7,8} requires a transition state in which the migration origin and terminus are bound to opposite faces of the migrant carbon (C_m). The resulting rehybridization of C_m would change its substituent-binding σ orbitals from approximately sp^2 in the reactant to approximately sp in the transition state, a process that would be unfavorable when the substituents are electronegative.⁹ Nevertheless, we now find that bicyclo[3.2.1]oct-2-en-7-one (**1**) undergoes a thermal degenerate rearrangement, which is most readily interpreted as a [1,3] acyl shift.

An optically active, deuterium labeled sample of ketone **1** can be separated by preparative gas chromatography from its isomer **2**. The mixture of **1** and **2** is obtained by application of a known^{10,11} ring expansion sequence to optically active norborn-5-en-2-one (**3**), which in turn can be prepared efficiently by the steps shown in Scheme I. The configurations and enantiomeric purities (E.P.) are absolute as shown.^{14,15}

Pyrolysis of (+)-**1-3-d** in the gas phase above 340 °C results in a degenerate rearrangement to (-)-**1-1-d** which can be observed by a combination of proton and ¹³C NMR spec-



troscopy and polarimetry. The chemical shifts of the olefinic protons (H_2 and H_3) of undeuterated **1** are very similar, even