

Figure 5. Schematic description of the behavior of **1** in aqueous and micellar environments.

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(12) N. I. H. Predoctoral Fellow 1970–1973.

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Carbon-Carbon Bond Cleavage and Iminocarbene Formation in the Thermal Decomposition of 2H-Azirines

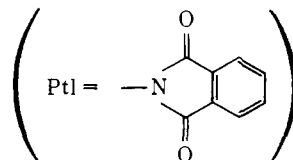
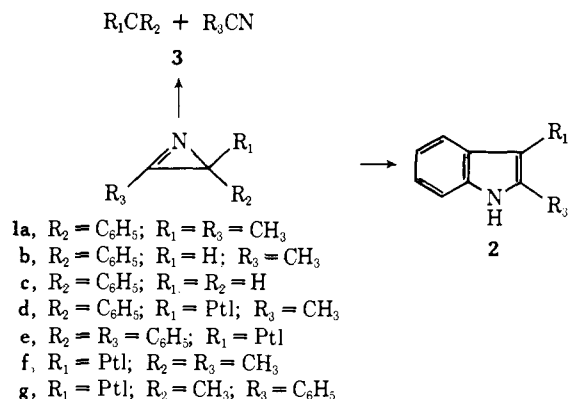
Sir:

Products formed on thermal decomposition of 2H-azirines (**1**) appear always to involve C–N rather than C–C bond cleavage.¹ In some cases (e.g., **1f**, **1g**)^{1a,b} this leads ultimately to fragmentation *via* carbene **3** and in other cases (e.g., **1b–1e**) to indole (**2**)^{1a,d} or pyrrole^{1e} formation (Scheme I). We now wish to report the discovery of C–C bond cleavage in the thermolysis of 2H-azirines and the formation of products previously unobserved in both thermal¹ and photochemical² azirine decompositions. We also present an explanation for the dependence of decomposition pathway upon substitution.

(1) (a) D. J. Anderson, T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 550 (1973); (b) T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *ibid.*, 555 (1973); (c) K. Isomura, S. Kobayashi, and H. Taniguchi, *Tetrahedron Lett.*, 3499 (1968); (d) K. Isomura, M. Okada, and H. Taniguchi, *ibid.*, 4073 (1969); (e) K. Isomura, M. Okada, and H. Taniguchi, *Chem. Lett.*, 629 (1972); (f) T. Nishiwaki, *J. Chem. Soc., Chem. Commun.*, 565 (1972); (g) R. Selvarajan and J. H. Boyer, *J. Heterocycl. Chem.*, 87, (1972); (h) T. Nishiwaki, A. Nakano, and H. Matsuoka, *J. Chem. Soc. C*, 1825 (1970); (i) J. H. Bowie and B. Nussey, *Chem. Commun.*, 1565 (1970); (j) D. Knittel, H. Hemetsberger, R. Leipert, and H. Weidmann, *Tetrahedron Lett.*, 1459 (1970); (k) N. S. Narasimhan, H. Heimgartner, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 56, 1351 (1973).

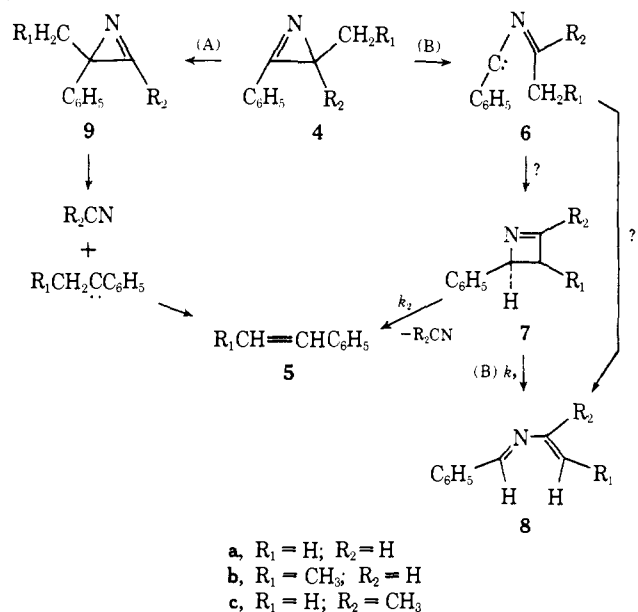
(2) Irradiation of 2H-azirines usually involves C–C bond cleavage but leads to products different from those observed here: (a) A. Padwa and J. Smolanoﬀ, *J. Amer. Chem. Soc.*, 93, 548 (1971); (b) M. Märky, H.-J. Hansen, and J. Schmid, *Helv. Chim. Acta*, 54, 1275 (1971); (c) W. Sieber, P. Gilgren, S. Chaloupka, H.-J. Hansen, and H. Schmid, *ibid.*, 56, 1679 (1973); (d) T. Nishiwaki, T. Kitamura, and A. Nakano, *Tetrahedron*, 26, 453 (1970); (e) F. P. Woerner and H. Reimlinger, *Chem. Ber.*, 103, 1908 (1970); (f) A. Padwa, S. Clough, M. Dharan, J. Smolanoﬀ, and S. I. Wetmore, Jr., *J. Amer. Chem. Soc.*, 94, 1395 (1972); (g) J. H. Boyer and G. J. Mikol, *J. Heterocycl. Chem.*, 1325 (1972); (h) A. Padwa, M. Dharan, J. Smolanoﬀ, and S. I. Wetmore, Jr., *J. Amer. Chem. Soc.*, 95, 1945 (1973).

Scheme I



2-Phenyl-3-methyl-2H-azirine³ (**4a**), when subjected to flow pyrolysis in the gas phase at 565° and 1 atmosphere pressure of helium (contact time ~10 sec), gave only 2% fragmentation to benzonitrile.^{1a} Rather, the major products were *styrene* (**5a**, 56% isolated yield), a reddish polymer, and (we presume) HCN. Similarly, 2-phenyl-3-ethyl-2H-azirine³ (**4b**) gave only 2% benzonitrile but 42% *cis*- and *trans*- β -methylstyrene (**5b**). Formation of these products requires bonding, at some point in the reaction, between C-2 of the azirine ring and the carbon attached to C-3. However, neither of the two most obvious mechanisms for achieving this (paths A and B illustrated in Scheme II) is particularly satisfying: (a) 1,3-shift (path A) is

Scheme II



- a, R₁ = H; R₂ = H
 b, R₁ = CH₃; R₂ = H
 c, R₁ = H; R₂ = CH₃

unprecedented in unsaturated three-membered rings; (b) hydrogen transfer in carbene **6** (path B, leading directly to **8**) should be much more favorable⁴ than C–H

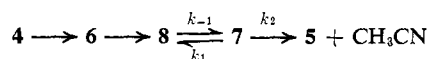
(3) Prepared *via* the vinylazide method; cf. A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, 90, 2869 (1968).

(4) (a) R. Srinivasan, *J. Chem. Soc. D*, 1041 (1971); (b) R. Srinivasan, *J. Amer. Chem. Soc.*, 91, 6250 (1969); (c) R. D. Streeper and P. D. Gardner, *Tetrahedron Lett.*, 767 (1973).

insertion to give **7**; and (c) azirine **7** (path B) should undergo cyclobutene-type ring opening⁵ to 1-phenyl-2-azabutadiene (**8**; *vide infra*) much more rapidly than retro 2 + 2 cleavage to styrene and HCN. A clue to what we believe is the true mechanism was obtained by examining the products of thermal decomposition (480°) of 2-phenyl-3,3-dimethyl-2*H*-azirine (**4c**). In this reaction, along with styrene (15%), benzonitrile (8%), and acetonitrile,⁶ was isolated a product (46%) of longer retention time. The new material exhibited pmr signals at δ 7.27–7.90 (5 H), 8.18 (1 H), 4.69 (1 H), 4.49 (1 H), and 2.00 (3 H) ppm. On the basis of this, mass spectral ($M^+ = m/e$ 145) and ir (intense band at 1644 cm^{-1}) data, it was assigned structure **8c**. The assignment was confirmed by hydrolysis of **8c** in aqueous mineral acid to benzaldehyde and acetone.

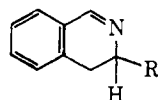
Subjection of **8c** to the azirine pyrolysis conditions gave styrene and acetonitrile, and this provided the key to the mechanism; we infer that the **7** \rightarrow **8** reaction is reversible. Such reversibility is consistent with the recent demonstration that cyclobutene is thermally accessible from butadiene.⁷ It also allows **7c** and **8c** to be intermediates in the pyrolysis of **4c** without requiring $k_2 > k_1$ and allows **8** to be formed directly by

Scheme III



1,4 hydrogen transfer⁴ from **6**. In addition, we have independently prepared 3-phenyl-2,3-dimethyl-2*H*-azirine⁸ (**9**, Scheme II) and subjected it to the pyrolysis conditions. This material rearranges only to indole **2** ($R_1 = R_3 = \text{CH}_3$). The lack of detectable styrene formation rigorously rules out the operation of path A in the decomposition of **4c**.

Thermal decomposition of either **4c** or **8c** at somewhat higher temperature (540°) resulted in the disappearance of **8c** and formation of a new product, identified as 3-methyl-dihydroisoquinoline^{9a,b} (**10**). Thermolysis of **4a** at 580° gave the parent 3,4-dihydroisoquinoline (**11**). This provides evidence that, although the conversion of



10, R = CH₃
11, R = H

8a to styrene or polymer occurs rapidly enough during the 565° pyrolysis of **4a** to preclude its isolation, the imine is in fact an intermediate in this reaction as well.

We cannot rule out the occurrence of C–H insertion in intermediate **6**, but the observation of 1,4 hydrogen transfer in analogous vinylcarbenes^{4,10} indicates that

(5) L. A. Paquette, J. J. Wynratt, and R. Allen, Jr., *J. Amer. Chem. Soc.*, **92**, 1763 (1970).

(6) Acetonitrile was found to be somewhat unstable to the reaction conditions; although its yield is therefore uncertain, sufficient material was obtained for identification.

(7) L. M. Stephenson, R. V. Gemmer, and J. I. Brauman, *J. Amer. Chem. Soc.*, **94**, 8620 (1972).

(8) Prepared by the method of (a) R. F. Parcell, *Chem. Ind. (London)*, 1396 (1963); see also (b) N. J. Leonard and B. Zwanenburg, *J. Amer. Chem. Soc.*, **89**, 4456 (1967).

(9) (a) V. M. Potapov, V. M. Dem'yanovick, L. D. Solov'eva, and A. P. Terent'ev, *Dokl. Akad. Nauk SSSR*, **185**, 614 (1969); (b) U. P. Basu and B. Bhattacharya, *J. Org. Chem.*, **32**, 4108 (1967); (c) S. Ikegami and S. Yamada, *Chem. Pharm. Bull.*, **14**, 1389 (1966).

(10) E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, *J. Amer. Chem. Soc.*, **95**, 5680 (1973).

our results are best accommodated by the modified mechanism outlined in Scheme III.¹¹ With regard to the variable mode of azirine thermal decompositions,¹ we suggest that the presence of a stabilizing group (such as phenyl) at C-2 tends to induce the formation of products formed from C–C cleavage,¹² whereas its location at C-3 (*cf.* compounds **1a–1e**) results in products formed by initial rupture of the inherently weaker C–N bond. We believe that product formation reflects true bond-cleavage preferences because no imine analogous to **8** is apparently formed in the thermolysis of **1a**. However, confirmation of that inference awaits experiments (such as those carried out in the analogous cyclopropene system¹⁰) designed to directly determine the rate-determining step in azirine pyrolysis.

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(11) In solution photochemical studies,² a nitrile ylide structure is most often written for **6**. While it is quite possible that such a structure is most reasonable for the C–C cleavage intermediate formed in solution, the general avoidance of charge-separated structures in the gas phase and the distinctive chemical behavior of **6** suggest that it is best thought of here as an iminocarbene.

(12) Both pathways outlined in Scheme I are consistent with this picture; apparently the carbene-stabilizing phthalimido group induces the subsequent step in **1d–1g** to be C–C cleavage leading to **3**, while in **1a–1c**, the "nitrene" nitrogen attacks the phenyl ring in a second step to give **2**.

(13) Camille and Henry Dreyfus Teacher-Scholar Grant Awardee, 1970–1975.

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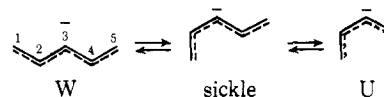
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Direct Observation of Acyclic Pentadienyllithium Conformational Isomers by Carbon-13 Magnetic Resonance Spectroscopy

Sir:

Pentadienyl anions could exist in three planar conformations, W, sickle, and U. Previous attempts to



detect more than one conformer of pentadienyl anions in low temperature pmr spectra failed in all but one case, 2-methylpentadienyllithium, in which two conformers were observed in the pmr spectrum at -20° but no conformational assignment could be made.¹ However, by comparison of pmr spectra of acyclic pentadienyllithiums to those of rigid sickle and U-shaped analogs, it was concluded that a proton-proton coupling constant, J_{23} ,² of ~ 12 Hz corresponded to a trans conformation and a coupling constant of ~ 6.5 Hz corresponded to a cis conformation of an inner bond of a pentadienyl anion.¹ On this basis acyclic pentadienyllithiums in ethers^{1,3} and acyclic pentadienyl-

(1) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967).

(2) Subscripts refer to protons bound to the corresponding numbered carbon atoms of the pentadienyl anions.

(3) S. Brenner and J. Klein, *Isr. J. Chem.*, **7**, 735 (1969).