financial support, and to Mr. David Eaton for stimulating discussions.

---

[18] National Science Foundation Predoctoral Fellow, 1967–1971.

[19] Alfred P. Sloan Foundation Fellow, 1970–1972; Camille and Henry Dreyfus Foundation Teacher–Scholar Grant Awardee, 1970–1975.

David H. White,[18] Paul B. Condit, Robert G. Bergman*[19]
Contribution No. 4353
Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91109

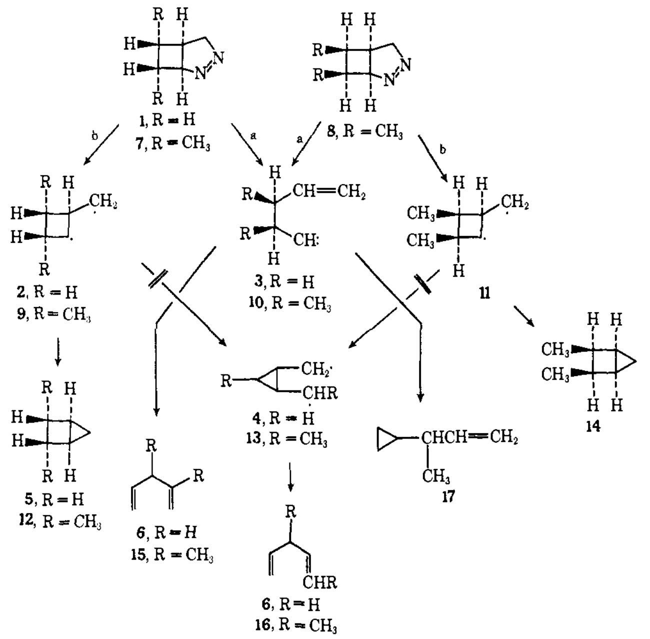
Received October 14, 1971

Evidence for Competitive Carbene and Diradical Pathways in the Thermal Decomposition of 6,7-Dimethyl-2,3-diazabicyclo[3.2.0]hept-2-enes. Absence of a "Di-π-methane" Pathway

Sir:

Both thermal and photochemical decomposition of 2,3-diazabicyclo[3.2.0]hept-2-ene (**1**) led to six products,[1] predominant among which were bicyclopentane (**5**) and 1,4-pentadiene (**6**). Two possible routes (Scheme I) for formation of **5** and **6** involve (a) carbene **3** (possibly formed *via* the corresponding diazo compound or by fragmentation of diradical **2**) and (b) the "di-π-methane" pathway[2] passing formally through diradicals **2** and **4**.

Scheme I



As is outlined in Scheme I, the stereochemistry and double position labeling inherent in dimethyl derivatives **7** and **8** are capable of distinguishing these two pathways. Formation of diene by path a would lead[3] to **15**, but path b predicts that **16** will arise; dimethylbicyclopentanes formed directly from diradicals **9** and **11** (path b) will have retained the initial syn or anti stereochemistry of their precursors, whereas any intervention of carbene **10** should produce stereochemical scrambling. We therefore have investigated the products formed on thermal decomposition of pyrazolines **7** and **8**.

Addition of diazomethane to *cis*-3,4-dimethylcyclobutene[4] in ether solution proceeded more slowly than in the parent case, but after 13 days at room temperature >87% of the olefin was consumed and two products (7:3 ratio) were observable by gas–liquid chromatography (glc). The major product was identified as the anti 1,3-dipolar cycloadduct **7** and the minor product as the syn (**8**) by observing the larger shifts of the methyl groups in **8** caused by complexation with Eu(fod)$_3$ in CCl$_4$ solution.[5]

Isomers **7** and **8** can be separated by preparative glc on a glass column. As in the parent case, thermal decomposition of each gave rise predominantly to diene, but also to cyclopropane and bicyclopentane products (Table I). With regard to the latter, both dimethylbicyclopentanes[6] **12** and **14** (Scheme I) were formed at 300°, but control experiments showed that the two isomers interconvert thermally at this temperature.[7] At 278°, where only very slow interconversion occurs, **7** gave rise to <1% **14** and **8** produced <1% **12**. The diene product, however, proved[8] *to be* **15**; less than 0.1% of **16**[9] was detectable in the reaction mixture.

Table I. Products Formed in the Thermal Decomposition of *syn*- and *anti*-6,7-Dimethyl-2,3-diazabicyclo[3.2.0]hept-2-enes[a]

Starting material and conditions	Products, %				
	12	14	15	17	Other[d]
7, flow system,[b] 278°	13.1	<1	56.8	23.2	6.8
8, flow system,[b] 278°	<1	10.1	52.8	28.4	8.6
7, flow system,[b] 300°	8.2	6.4	54.2	21.6	9.7
8, flow system,[b] 300°	5.2	9.6	50.5	21.7	12.9
7, injector port,[c] 280°	20.3	0.8	45.5	24.4	8.3
7, injector port,[c] 305°	19.0	3.8	43.6	22.0	10.4
7, injector port,[c] 342°	15.6	9.2	40.2	20.7	12.2
7, injector port,[c] 378°	15.7	11.5	36.0	17.3	12.8

[a] All pyrolyses carried out in the gas phase. [b] Quartz tube; contact time 70 sec. [c] Injector port of a Hewlett-Packard 5750 gas chromatograph equipped with electronic digital integrator. Percentages reproducible to ±1.0%. [d] Tentatively assigned as *cis*-2,3-dimethyl-1-methylenecyclobutane.

These data implicate the carbene (path a) as a precursor to diene (to the complete exclusion of path b), but rigorously rule it out as an intermediate in the formation of the dimethylbicyclopentanes. The formation[10] of C–H insertion product **17** constitutes

---

[1] D. H White, P. C. Condit, and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 1348 (1972).

[2] See footnote 10 of ref 1.

[3] 1,2-Hydrogen rearrangement and C–H insertion should be the most rapid reactions of carbene **3**: see, for example, (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 3; and (b) W. Kirmse, "Carbene, Carbenoide, und Carbenanaloge," Verlag Chemie, Weinheim, 1969, Chapter 6.

[4] Prepared by decomposition of *cis*-3,4-dimethylcyclopropanecarboxaldehyde *p*-toluenesulfonylhydrazone in base (D. H. White and R. G. Bergman, unpublished results); properties of the hydrocarbon agreed with those reported by earlier workers: (a) R. E. K. Winter, *Tetrahedron Lett.*, 1207 (1965); (b) R. Srinivasan, *J. Amer. Chem. Soc.*, **91**, 7557 (1969).

[5] See, for example, R. E. Rondeau and R. E. Sievers, *ibid.*, **93**, 1522 (1971).

[6] J. A. Berson, W. Bauer, and M. M. Campbell, *ibid.*, **92**, 7515 (1970). We are grateful to Professor Berson and Dr. Bauer for supplying spectral and synthetic data on compounds **12** and **14**.

[7] All other products, as well as **16**, were shown to be stable to the pyrolysis conditions.

[8] N. F. Cywinski, *J. Org. Chem.*, **30**, 361 (1965).

[9] T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **87**, 5638 (1965).

[10] Identified by comparison with an authentic sample prepared by reaction of Zn and CH$_2$I$_2$ with 3-methyl-1,4-pentadiene purchased from Chemical Samples Co., Columbus, Ohio.

additional persuasive evidence[3] for the competitive intermediacy of **10**, and the fact that the relative amounts of **15** and **17** formed from **7** and **8** are very similar is also consistent with their formation from a common intermediate. Finally, the temperature dependence of the rates of carbene-derived and diradical-derived product observed in the parent system[1] is also found in the dimethyl series.[11]

In summary, our results are best rationalized by the postulate that pyrazolines of general structure **1** undergo dual pathway decomposition.[12] The major route involves rate-determining carbene formation, followed by rapid reaction of this material to give characteristic hydrogen-shifted and insertion products. The minor route involves direct nitrogen loss and subsequent bicyclopentane formation, presumably *via* substituted 1,3-diradicals.

Acknowledgments. We are grateful to the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

[11] A plot of the log of the ratio of radical-derived to carbene-derived products is linear and gives $\Delta E_a = 5.24$ kcal/mol and $\Delta\Delta S^{\ddagger} = +3.38$ eu.

[12] Once again, for the reasons stated in footnote 11 in ref 1, we consider an open-chain diazo compound, formed *via* retro-1,3-dipolar reaction of **7** and **8**, the most likely source of carbene 10.

[13] National Science Foundation Predoctoral Fellow, 1970–present.

[14] (a) Alfred P. Sloan Foundation Fellow, 1970–1972; (b) Camille and Henry Dreyfus Foundation Teacher–Scholar Grant Awardee, 1970–1975.

Robert A. Keppel,[13] Robert G. Bergman*[14]
Contribution No. 4354
Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91109

Received October 14, 1971

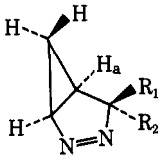
Multiple Mechanisms in the Thermal and Photochemical Decomposition of 2,3-Diazabicyclo[3.1.0]hex-2-enes

Sir:

We report the synthesis and decomposition of several bicyclic azo compounds designed as precursors to "cyclopropylmethylene" diradicals[1] of the type **1**. We believe that the results reported here (as in the accompanying communications)[2] provide notable exceptions to the generally observed reaction modes of bicyclic azo compounds.

1

Addition of cyclopropene[3] to a pentane solution of diazoethane at −78° yielded a 60:40 mixture of *exo*- and *endo*-4-methyl-2,3-diazabicyclo[3.1.0]hex-2-ene (**2a** and **2b**, respectively) as a pale yellow oil. The epimeric mixture was separated by preparative vpc (10 ft × 3/8 in., glass, UC-W98, 20% on HMDS Chromosorb W; 55°). Compound **2a** exhibits the following spectral characteristics: *m/e* 96 (4%), 68 ($M^+ - N_2$, 42%), 67 (base peak); nmr (60 MHz, CCl_4 containing 2% $CHCl_3$) δ 4.66 (1 H, mult), 4.24 (1 H, d of q, $J = 7.3$, 3.0 Hz), 2.8–0.9 (2 H, complex mult), 1.33 (3 H, d, $J = 7.3$ Hz), −0.19 (1 H, mult); ir $\nu_{\max}^{\text{film}}$ 1515 (N=N), 1030 cm^{-1}; uv $\lambda_{\max}^{\text{hexane}}$ 328 nm (ϵ 335). Compound **2b** shows: *m/e* 96 (5%), 68 (37%), 67 (base); nmr (60 MHz, CCl_4 containing 2% $CHCl_3$) δ 5.0–4.5 (2 H, complex mult), 1.60 (1 H, mult), 1.47 (3 H, d, $J = 7.3$ Hz), 0.89 (1 H, mult), −0.17 (1 H, mult); ir $\nu_{\max}^{\text{film}}$ 1514, 1028 cm^{-1}; uv $\lambda_{\max}^{\text{hexane}}$ 330 nm (ϵ 149). The 220-MHz nmr spectra of **2a** and **b** are pseudo-first-order and can be satisfactorily analyzed, establishing the indicated stereochemistry unequivocally; in **2a** the vicinal H_a–H_b coupling constant is 1.3 Hz, whereas $J_{H_a-H_c}$ is 6.5 Hz in **2b**.[4]

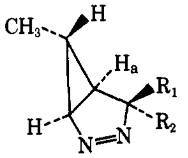


2a, $R_1 = H_b$; $R_2 = CH_3$
2b, $R_1 = CH_3$; $R_2 = H_c$

Sealed tube pyrolysis (vapor or liquid phase) of **2a** at 119°, or irradiation (3130 Å, pentane), resulted in clean formation of *trans*-1,3-pentadiene (*t*-**3**) (98%) and *cis*-1,3-pentadiene (*c*-**3**) (2%).[5] Decomposition of **2b** under identical conditions produced 3% *t*-**3** and 97% *c*-**3**. No change in product ratios was observed on thermolysis of **2a** or **b** in apparatus packed with glass helices. The ratio of the first-order rate constants for pyrazoline disappearance at 119°, k_{2a}/k_{2b}, was found to be 30, while quantum yields for 3130-A induced pyrazoline decomposition were 0.75 (**2a**) and 0.53 (**2b**).[6]

The unusual rate ratio and product selectivity exhibited by pyrazolines **2** suggest that mechanisms other than diradical may obtain. We have prepared pyrazolines **4** to gain further mechanistic insight.

Addition of diazoethane to 3-methylcyclopropene[7] at −78° afforded *exo*-4,*exo*-6-dimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene (**4a**) and the endo 4 epimer **4b**. The stereochemistry assigned at C_4 is supported by the nmr spectra (100 MHz): in **4a**, $J_{H_a-H_b} = 2.3$ Hz, and $J_{H_a-H_c} = 7.1$ Hz (**4b**). All other spectral characteristics of **4** are consistent with the proposed structure.



4a, $R_1 = H_b$; $R_2 = CH_3$
4b, $R_1 = CH_3$; $R_2 = H_c$

Pyrolysis or photolysis of **4a** or **b** gave mixtures of C_6H_{10} hydrocarbons (Scheme I). The nature of the decomposition products strongly suggests the intervention of carbenes **5a** and **5b**, visualized as arising *via* the mechanism shown in Scheme I. We have pre-

---

[1] (a) R. Srinivasan, *J. Amer. Chem. Soc.*, **90**, 4498 (1968); (b) J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970).

[2] (a) D. H. White, P. B. Condit, and R. G. Bergman, *ibid.*, **94**, 1348 (1972); (b) R. A. Keppel and R. G. Bergman, *ibid.*, **94**, 1350 (1972).

[3] G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966).

[4] We wish to thank Professor Robert S. Cooke for assistance in analyzing the 220-MHz spectra of 2.

[5] The dienes were identified by spectral and vpc comparison with authentic samples. The absolute diene yield was 86%.

[6] Blue fluorescence ($\lambda_{\max}$ 430 nm) with an onset at 365 nm (~78 kcal/mol) was observed from a degassed pentane solution of a 3:2 mixture of **2a** and **2b**.

[7] R. Köster, S. Arora, and P. Binger, *Angew. Chem., Int. Ed. Engl.*, **9**, 810 (1970).