(30% yield) to which we assign the tentative structure **8**, and we also observed the reaction of **5** with benzaldehyde to give a substance $C_{26}H_{22}O_4$ (30%) believed to be **9**.[11] Reasonable pathways to these unexpected products are shown. The failure of **5** to undergo the concerted cycloaddition is attributed to its high nucleophilicity, which evidently exceeds that of 1,3 dipoles by far.

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(11) Assignments are based on spectral and analytical data. Details are to be reported elsewhere.

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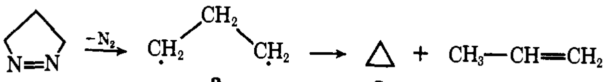
Formation of 1,4-Pentadiene and Vinylcyclopropane in the Thermal and Photochemical Decomposition of 2,3-Diazabicyclo[3.2.0]hept-2-ene

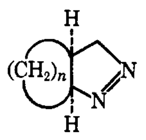
Sir:

Pyrazolines (*e.g.*, **1**) normally undergo thermal[1] and photochemical[2] decomposition to form cyclopropanes (**3**) and olefins (**4**), presumably *via* the intermediacy of



1 2 3 4

"trimethylene" diradicals such as **2**. Although the detailed structure of **2** is still a matter of some discussion,[3] the cyclopropane–olefin product pattern is observed in a large number of substituted systems. These include bicyclic pyrazolines such as **5** (n = 3) which probably[4] react initially *via* intermediate **6**



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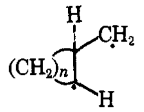
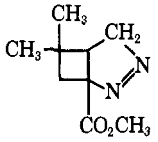


6

However, data for the case of **5** (n = 2), which should generate diradical **17** (*vide infra*), are somewhat confusing. One substituted derivative, **7**, gave typical bicyclopentane and olefin products,[5] although on photolysis it was reported to form a "complex product mixture." Another system, **8**, decomposed to both bicyclopentane and substituted 1,4-pentadienes on irradiation; no thermal decomposition was reported.[6] Compound **9** produced 1-carbomethoxybicyclo[2.1.0]pentane "and five other [unidentified] products" when heated.[7] Addition of carbenes and carbenoids to substituted cyclobutenes (which might directly generate diradicals of general structure **6** (n = 2)) has been reported to give dienes, bicyclopentanes, and vinylcyclopropanes as well as other products.[8] Because these systems appear to behave so differently, we felt that a careful study of the thermal and photochemical decomposition of the parent molecule **10** was warranted. We herein report the results of such a study.



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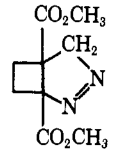

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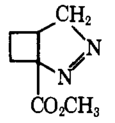

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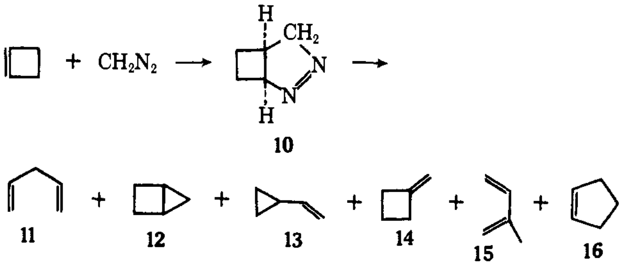
Addition of diazomethane to cyclobutene in pentane solution at room temperature produced a 76% yield of 1,3-dipolar addition product **10** after 4 days. Compound **10** was purified by gas–liquid chromatography (glc); its properties and spectral data (ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1540 cm^{-1}; uv $\lambda_{\max}^{\mathrm{MeOH}}$ 323 nm (ϵ 338); nmr δ (CCl_4) 1.0–3.0 (complex absorption, 5 H), 4.38 (mult, 2 H), 5.06 (mult, 1 H)) were consistent with the structure assigned by earlier workers.[9] Gas-phase thermal decomposition in a quartz flow system or in the injector port of a glc instrument gave rise to six products (88% yield), **11–16**, in the proportions listed in Table I. Somewhat surprisingly, direct irradiation of **10** (Pyrex vessels) in pentane solution increased the relative amount of bicyclopentane formed, and photosensitized decomposition resulted in an even larger proportion of **12**.



10

11 12 13 14 15 16

The formation of **11** as a major product in the thermal decomposition is unprecedented. Its presence, along with that of vinylcyclopropane (**13**), raises the possibility that diradical **17**, a potential initial intermediate, may be in equilibrium with an isomeric "di-π-methane" intermediate[10] formally written here as diradical **18**.

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(1) (a) R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **88**, 3963 (1966); (b) R. J. Crawford and D. Cameron, *ibid.*, **88**, 2589 (1966); (c) R. J. Crawford and G. L. Erickson, *ibid.*, **89**, 3907 (1967); (d) R. J. Crawford and L. J. Ali, *ibid.*, **89**, 3908 (1967); (e) A. Mishra and R. J. Crawford, *Can. J. Chem.*, **47**, 1515 (1969); (f) D. E. McGreer, R. S. McDaniel, and M. J. Vinje, *ibid.*, **43**, 1389 (1965); (g) D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *ibid.*, **43**, 1407 (1965); (h) D. E. McGreer, N. W. K. Chiu, and M. G. Vinje, *ibid.*, **43**, 1398 (1965); (i) D. E. McGreer and W.-S. Wu, *ibid.*, **45**, 461 (1967); (j) B. H. Al-Sader and R. J. Crawford, *ibid.*, **46**, 3301 (1968); (k) W. R. Roth and M. Martin, *Tetrahedron Lett.*, 3865 (1967); (l) A. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **89**, 7133 (1967); (m) W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967); see also, (n) *Justus Liebigs Ann. Chem.*, **702**, 1 (1967).

(2) (a) R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, **46**, 3305 (1968); (b) K. B. Wiberg and A. deMeijere, *Tetrahedron Lett.*, 59 (1969).

(3) See, for example, (a) R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969); (b) R. Hoffmann, *ibid.*, **90**, 1475 (1968); (c) L. Salem, *Accounts Chem. Res.*, **4**, 322 (1971); (d) L. Salem and C. Rowland, *Angew. Chem.*, in press; (e) K. Q. Siu, W. M. St. John, and E. F. Hayes, *J. Amer. Chem. Soc.*, **92**, 7249 (1970); (f) J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *ibid.*, **94**, 282 (1972).

(4) (a) P. B. Condit and R. G. Bergman, *Chem. Commun.*, 4 (1971); (b) M. P. Schneider and R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970).

(5) T. H. Kinstle, R. L. Welch, and R. W. Exley, *J. Amer. Chem. Soc.*, **89**, 3660 (1967).

(6) M. Franck-Neumann, *Tetrahedron Lett.*, 2979 (1968).

(7) P. G. Gassman and K. T. Mansfield, *J. Org. Chem.*, **32**, 915 (1967).

(8) (a) C. S. Elliott and H. M. Frey, *Trans. Faraday Soc.*, **64**, 2352 (1968); (b) H. M. Frey, *Chem. Commun.*, 260 (1965); (c) N. C. Yang and T. A. Marolewski, *J. Amer. Chem. Soc.*, **90**, 5644 (1968).

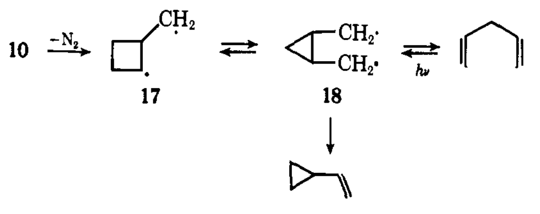
(9) H. Paul, I. Lange, and A. Kausmann, *Chem. Ber.*, **98**, 1789 (1965).

(10) (a) For references to a number of examples of the di-π-methane rearrangement, see H. E. Zimmerman and P. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969). For other examples and mechanistic studies, see (b) H. E. Zimmerman and A. A. Baum, *ibid.*, **93**, 3646 (1971); (c) H. E.

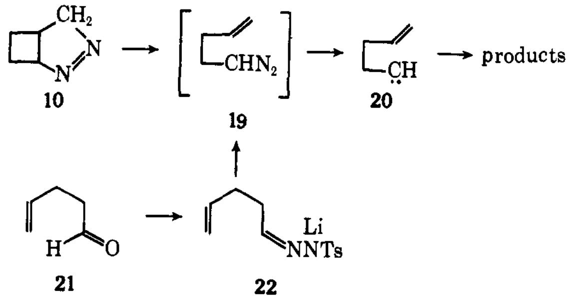
Table I. Products Formed on Decomposition of 2,3-Diazabicyclo[3.2.0]heptene-2 (**10**) and 4-Pentenal *p*-Toluenesulfonylhydrazone Lithium Salt (**22**)

Starting material	Conditions	Products, %						
		11	**12**	**13**	**14**	**15**[d]	**16**[d]	Other
10	297°, gas phase[a]	72.0	15.1	5.9	2.1	2.5	2.3	
10	267°, gas phase[b]	75.3	14.5	6.1	1.9	2.1	0.2	
10	290°, gas phase[b]	73.5	15.4	6.0	2.2	2.7	0.3	
10	339°, gas phase[b]	69.5	17.1	6.3	2.7	3.3	1.0	
10	389°, gas phase[b]	64.7	15.9	6.5	3.6	4.1	5.2	
10	321°, gas phase[b,c]	71.2	16.7	6.1	2.7	2.9	0.3	
10	*hν*, cyclohexane $\lambda > 3000$ nm	26.8	58.9	10.7	0.9	1.8[f]	0.7	
10	*hν*, cyclohexane, acetophenone	10.3	89.7	Trace	Trace	Trace	Trace	
22	251°, tetraglyme[b]	92.2	0	3.8	0	0	0	4.0[e]
22	335°, tetraglyme[b]	88.7	0	6.0	0	0	0	5.5[e]

[a] Flow system, atmospheric pressure, contact time = *ca.* 20 sec. [b] Pyrolysis carried out in injector port of Hewlett-Packard glc instrument equipped with electronic digital integrator. Percentages are reproducible to ±0.2 absolute %; where zero percentages are listed, ≥0.1% was detectable. [c] Injector port packed with glass chips. [d] Compound **15** is probably formed from thermal rearrangement of 1-methylcyclobutene. The small amounts of **16** observed probably arise from thermolysis of **12**; kinetic studies reported earlier (C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Amer. Chem. Soc.*, **86**, 679 (1964)) are consistent with slight conversion of **12** to **15** under our pyrolysis conditions. Appropriate control experiments demonstrated that all the other products are stable to the pyrolysis conditions. [e] Mainly piperylenes, which Kirmse and Grassmann have indicated[12] are formed in a competing cationic pathway. [f] 1-Methylcyclobutene.



Among other mechanistic alternatives, however (such as direct formation of **13** from **17**), is one which may not involve 1,3 diradicals; **10** may first undergo a reverse 1,3-dipolar addition[11] to diazo compound **19**, which decomposes *via* carbene **20** to **11**, **13**, and possibly **12**. In order to investigate this possibility, we prepared the *p*-toluenesulfonylhydrazone lithium salt (**22**) of 4-pentenal (**21**) and examined the products[12] of its thermal decomposition. As is outlined in Table I, **22** gave rise to 1,4-pentadiene and vinylcyclopropane; no **12**, **14**, or **15** was formed. These data indicate that carbene **20** may be an intermediate[13] in the formation of **11** and **13**. They also suggest that **20** is not an intermediate[14] in the formation of bicyclopentane, but the intervention of different electronic states of **20** in the two reactions cannot be ruled out. The dual pathway hypothesis is, however, supported by the appreciable (and unusual[1a]) temperature dependence of the product distribution (Table I); as the temperature is raised, the percentage of carbene-type products **11** and **13** decreases with respect to diradical-type products **12**, **14**, **15**, and **16**. A plot of the log of the yield ratio $[(\mathbf{12} + \mathbf{14} + \mathbf{15} + \mathbf{16})/(\mathbf{11} + \mathbf{13})]$ *vs.* $1/T$ is linear and gives $\Delta E_a = +3.3$ kcal/mol, $\Delta\Delta S^{\ddagger} = +3.2$ eu.



Our results are most interesting when compared with the observations of Elliott and Frey concerning the products formed on addition of methylene to cyclobutene.[8a] Although this reaction has also been suggested to proceed *via* diradical **17** the product distribution is significantly different from that observed in our work. The largest discrepancy is observed in the triplet reactions—the "triplet" product in the methylene addition is reported to be >80% vinylcyclopropane,[8a] whereas the presumed triplet generated by photosensitized decomposition of **10** gives bicyclopentane (**12**). If both reactions are truly triplet decompositions, it appears that two different triplet intermediates must be involved.[16]

A stereochemical and double-labeling test of the dual pathway mechanism for decomposition of azo compounds such as **10** is reported in the accompanying communication.[15]

Acknowledgments. We are grateful to the Petroleum Research Fund of the American Chemical Society for

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Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259 (1970); (d) W. G. Dauben and W. A. Spitzer, *ibid.*, **92**, 5817 (1970); (e) for an example in which apparent di-π-methane products were formed from an independent precursor, see L. D. Hess and J. N. Pitts, *ibid.*, **89**, 1973 (1967).

(11) A similar retro-1,3-dipolar reaction has been reported in a system where the diazo compound is isolable: M. Franck-Neumann and C. Buchecker, *Tetrahedron Lett.*, 2659 (1969). Our data do not rule out the possibility that carbene **20** arises directly from diradical **17**, as suggested by Franck-Neumann in ref 6; however, the temperature dependence of our product distribution and the fact that carbene–olefin additions are not normally thermally reversible suggest that the diazo compound route is more likely.

(12) The catalyzed decomposition of the diazo compound, generated *in situ*, has been examined: W. Kirmse and D. Grassmann, *Chem. Ber.*, **99**, 1746 (1966).

(13) It is possible, of course, that diene **11** is formed by *both* carbene and di-π-methane-type pathways.

(14) More conclusive evidence on this point is presented in the accompanying communication.[15]

(15) R. Keppel and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 1350 (1972).

(16) Srinivasan has shown[17] that *cis*-3,4-dimethylcyclobutene undergoes ring opening on mercury-sensitized decomposition. Elliott and Frey do not appear to have checked the stability of cyclobutene itself to their reaction conditions;[8a] if mercury-promoted ring opening to butadiene occurs, the vinylcyclopropane formed could arise from reaction of this diene with methylene.

(17) R. Srinivasan, *J. Amer. Chem. Soc.*, **91**, 7557 (1969).

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.

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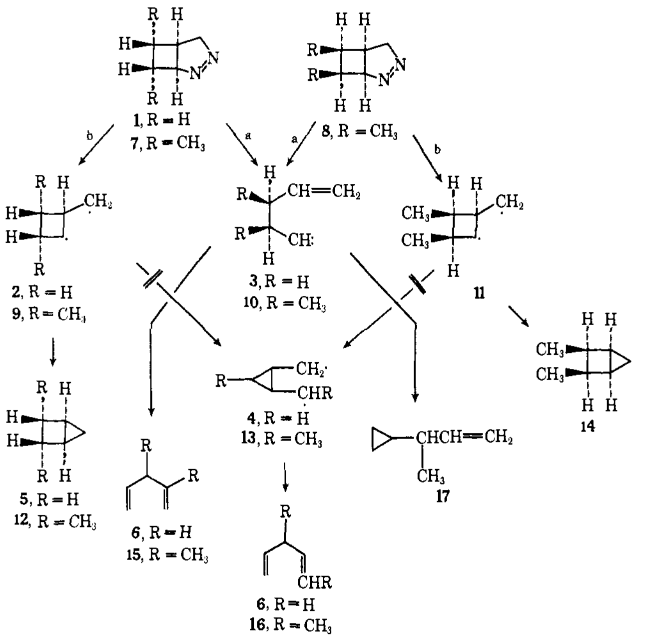
Evidence for Competitive Carbene and Diradical Pathways in the Thermal Decomposition of 6,7-Dimethyl-2,3-diazabicyclo[3.2.0]hept-2-enes. Absence of a "Di-π-methane" Pathway

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

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(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.