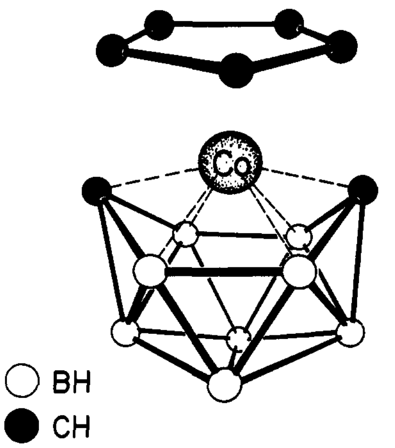

Figure 1. The proposed structure of $B_8C_2H_{10}CoC_5H_5$.

The major product resulting from treatment of 1,6-$B_8C_2H_{10}$ in THF at −78° with 2 equiv of sodium in the presence of a catalytic amount of naphthalene, followed by the addition of excess $CoCl_2$, was a green complex formulated as $Co(B_8C_2H_{10})_2^-$ (II). Complex *II* was isolated by column chromatography and recrystallized from acetone–water as its Cs^+ salt in 48% yield, mp 324° dec. *Anal.* Calcd for $[(B_8C_2H_{10})_2Co]^-Cs^+$: B, 39.96; C, 11.10; H, 4.62; Co, 13.61; Cs, 30.70; equiv wt, 433. Found: B, 40.07; C, 11.19; H, 5.00; Co, 13.14; Cs, 29.71; equiv wt, 457. The electronic spectrum determined in acetonitrile was [λ_{max}, mμ (ϵ)] 236 (28,000), 320 (16,100), 637[7] (155). The 32.1-MHz ^{11}B nmr spectrum of II was similar to that of I, having doublets of area ratio 1:2:1 at −8.9 (151), +7.5 (153), and +24.6 (136). The 60-MHz ^1H nmr spectrum contained a broad resonance at τ 4.57. These results suggest that the structure of the $B_8C_2H_{10}^{2-}$ ion in II is identical with that in I.

An X-ray diffraction study is planned to determine precisely the nature of the $B_8C_2H_{10}^{2-}$ ion. A number of additional products from these reactions are currently being investigated.

Acknowledgment. The authors wish to thank Dr. G. B. Dunks for helpful discussion. This research was supported in part by the Office of Naval Research and the Army Research Office (Durham).

(6) F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966).
(7) Broad, two overlapping unsymmetrical peaks.

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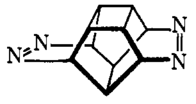
Received March 19, 1971

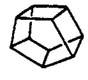
Synthesis and Reactions of 2,3,7,8-Tetraazahexacyclo[7.4.1.$0^{4,12}$.$0^{5,14}$.$0^{6,11}$.$0^{10,13}$]tetradeca-2,7-diene[1]

Sir:

The thermal and photoinduced decomposition of alkyl cyclic azo compounds has been a subject of considerable interest.[2] We wish to report the synthesis and reactions of a cyclic bisazo compound, 2,3,7,8-tetraazahexacyclo[7.4.1.$0^{4,12}$.$0^{5,14}$.$0^{6,11}$.$0^{10,13}$]tetradeca-2,7-diene (**1**), an attractive and potential precursor of the hitherto unknown pentaprismane[3] **2**.



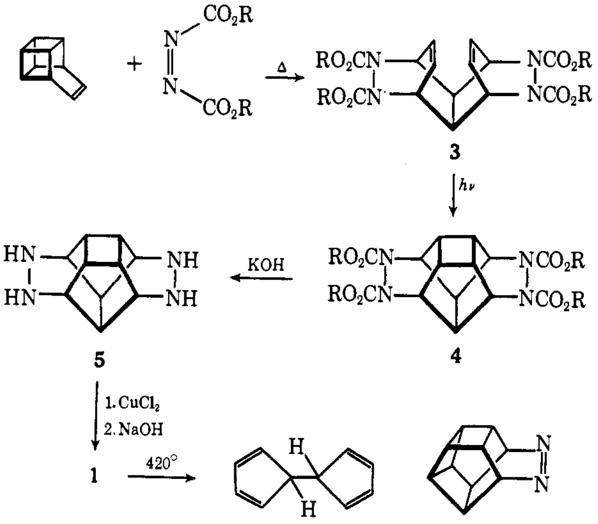
1



2

Reaction of pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]dec-9-ene[4] with diethyl azodicarboxylate (*cf.* Scheme I) (2.5:1 mole ratio) at 76° yielded the 2:1 adduct **3** in 85% yield: mp 190–191°; τ ($CDCl_3$) 3.5–6.2 (m, 4 H), 4.9–5.5 (m, 4 H), 5.77 (q, 8 H), 7.07 (broad S, 2 H), 8.75 (t,12 H).[5] When **3** was photolyzed in dry acetone (Vycor filter) for 5 hr, **4** was obtained in 90% yield: mp 155–156°; τ ($CDCl_3$) 5.72 (q, 8 H), 5.69 (under 5.7 quartet, 4 H), 7.00 (m, 6 H), 8.68 (t,12 H). Hydrolysis–decarboxylation of **4** with hot potassium hydroxide in methanol gave hydrazine **5**. Treatment of **5** with cupric chloride in water gave a dark brick red cuprous chloride complex of **1**. Bisazo compound **1** was generated by dissolving the cuprous complex in alkaline aqueous solution and extracting with chloroform (60% yield; mp 320° (sealed tube); τ ($CDCl_3$) 4.32 (m, 4 H), 7.52 (m, 4 H), 8.24 (m, 2 H); ν_{max}^{KBr} 1518 cm^{-1} (–N=N–); $\lambda_{max}^{CH_3CN}$ 360 mμ (ϵ ~540)).

Scheme I



Compound **1** was thermally stable ($t_{1/2}$ = 0.53 hr at 250°). Flash vacuum pyrolysis (FVP) of **1** at 420° gave 9,10-dihydrofulvalene[6] as the only identifiable

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(1) K. W. Shen and L. J. Winters, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstract ORGN 57.

(2) (a) P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968); (b) E. L. Allred and R. L. Smith, *ibid.*, **89**, 7311 (1967); (c) *ibid.*, **91**, 6766 (1969); (d) W. R. Roth and M. Martin, *Tetrahedron Lett.*, **39**, 3865 (1967); (e) J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **91**, 777 (1969); (f) C. G. Overberger and J. W. Stoddard, *ibid.*, **92**, 4922 (1970); (g) P. D. Condit and R. G. Bergman, *Chem. Commun.*, 4 (1971); (h) R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970); (i) P. S. Engel and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 5883 (1970), and references cited in these papers.

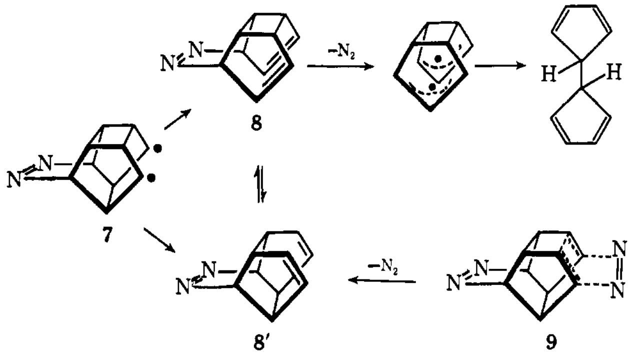
(3) H. P. Schultz, *J. Org. Chem.*, **30**, 1361 (1965).

(4) (a) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Lett.*, 1017 (1966); W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966); (b) E. LeGoff and S. Oka, *J. Amer. Chem. Soc.*, **91**, 5665 (1969); H. H. Westberg, E. N. Cain, and S. Masamune, *ibid.*, **91**, 7512 (1969).

(5) After hydrolysis–decarboxylation of **3**, followed by oxidation with mercuric oxide, *cis*-9,10-dihydronaphthalene was obtained. This further confirms the structure of **3** as shown: K. W. Shen, *Chem. Commun.*, 391 (1971).

product based on the nmr spectrum of the pyrolysate; neither pentaprismane **2** nor the monozao compound **6** was obtained. This suggests that **6** may not be formed at all in the thermolysis of **1**. Instead a fragmentation process such as Scheme II is probably operative.

Scheme II



Compound **1** decomposes, plausibly by a concerted cleavage of C–N bonds,[7a] to the 1,4 diradical **7** which then undergoes a ring opening reaction yielding intermediate **8** and **8′**. The interconversion between **8** and **8′** is simply a reversible *cis*-1,2-divinylcyclobutane Cope rearrangement.[7b] The thermal instability of bis-allylic azo compounds **8** under the present FVP condition is due to the resonance stabilization of the bis-π-allylic radicals[7c,d] formed.

The mass spectrum of **1** further substantiates the above postulation. The mass spectrum (70 eV) of **1** exhibits the following peaks: *m/e* (%) 186 (parent, 44) 130 (15), 129 (100), 128 (70), 116 (8), 115 (84), 65 (32). Interestingly enough, no peak due to monoazo compound **6** is present (*i.e.*, *m/e* 158). The fragmentation pattern is closely related to the mass spectrum of 9,10-dihydrofulvalene, obtained by Schissel and Hedaya:[8] 130 (91), 129 (100), 128 (58), 116 (8), 115 (76), 65 (19), at 50 eV. This mass spectrum together with FVP results enables us to propose the reaction mechanism shown in Scheme II. It is particularly interesting to note that both reaction mechanisms proposed by Roth and Martin[7a] cannot be operative in **1** due to its rigid structure.

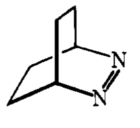
The formation of **8′** may take place in a concerted manner (a symmetry-allowed $-[{}_{\pi}2_{s} + {}_{\pi}2_{s} + {}_{\pi}2_{s}]$ process[9]) with participation of cyclobutane bonding electrons[10–13] in the product-forming transition state such as **9**. However, this possibility was ruled out on the basis of kinetic studies.

The kinetics of **1** were studied in thick-walled nmr tubes with acetonitrile-d_3 as solvent; the rate of decomposition of **1** was followed by nmr with benzene as internal standard. Fragmentation was found to be first order, with rates and activation parameters shown in Table I. Note that E_{act} for the decomposition of **1** is quite close to that for fragmentation of the bicyclic azo compound 2,3-diazabicyclo[2.2.2]oct-2-ene (**10**) in which no neighboring cyclobutane ring is present. On the other hand, despite their structural similarity, compounds **1** and **11** show a remarkable reactivity difference (relative rate 1:10^4 at 150°). These results strongly suggest that there is no participation of cyclobutane electrons in the rate-determining step in the thermal fragmentation of **1**. This may be due to the fact that the rigid cage structure in **1** does not allow the orbitals to have a better overlap in the transition state whereas for **11** a much better orbital overlap can be readily achieved due to the presence of a much more "flexible" cyclobutane ring as shown in **12**. The ground-state hydrogen–hydrogen interaction in **11** may also have significant contribution in lowering the activation energy.

Table I

Compd	$k \times 10^5$ sec^{-1}	Temp, °C	E_{act}, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate at 150°
1	1.18[a]	215			
	6.65	230			
	34.00	250	45.1 ± 0.4	+6.6	1
10	49.00	250	44.6 ± 0.2[b]	+10.5	7
11			39.2 ± 0.3[c]	+11[c]	10^4

[a] The rate constant of **1** has been divided by two due to the presence of two azo groups. [b] S. G. Cohen, R. Zand, and C. Steele, *J. Amer. Chem. Soc.*, **83**, 2895 (1961). [c] See ref 11.



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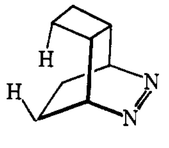

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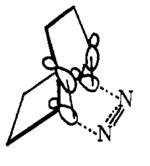

12

During our preparation of this manuscript, Allred and Johnson[14] reported the influence of geometry on

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(6) E. Hedaya, *Accounts Chem. Res.*, **2**, 367 (1969); E. Hedaya, D. W. McNeil, P. O. Schissel, and D. J. McAdoo, *J. Amer. Chem. Soc.*, **90**, 5284 (1968).

(7) (a) For a discussion of concertness of thermal decomposition of cyclic azo compounds, see ref 2b,c. Roth and Martin have advanced two explanations to account for the results of thermolysis of *exo*-2,3-diazabicyclo[2.2.1]hept-2-ene-*5,6-d*$_2$. Inversion of the stereochemistry of the product was ascribed to concerted elimination of nitrogen with accompanying backside p-orbital overlap in transition state (W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, 702, 1 (1967)). Later they proposed that fragmentation involved consecutive cleavage of the two C–N bonds with the backside p-orbital overlap (W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967); see also ref 2g). (b) *cis*-1,2-Divinylcyclobutane rearranges rapidly to 1,5-cyclooctadiene at 120°: E. Vogel, *Justus Liebigs Ann. Chem.*, **615**, 1 (1958). The conversion of **8′** to **8** is expected, since the two double bonds are properly oriented due to the cage structure. *cis*-1,2-Divinylcyclopentane and 1,5-cyclononadiene have been found to be in equilibrium at 220°. See E. Vogel, W. Grimme, and E. Dinne, *Angew. Chem.*, **75**, 1103 (1963). (c) C. G. Overberger, J-P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen–Nitrogen Bonds," Ronald Press, New York, N. Y., 1966. (d) B. H. Al-Sader and R. J. Crawford, *Can. J. Chem.*, **48**, 2745 (1970).

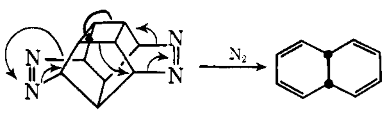
(8) Private communication from Drs. E. Hedaya and P. O. Schissel.

(9) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(10) The participation of cyclopropane rings in the transition state has been proposed and extensively studied in the thermolysis of cyclic azo compounds. See ref 2b–e: M. Martin and W. R. Roth, *Chem. Ber.*, **102**, 811 (1969); and H. Tanida and S. Teratabe, *Tetrahedron Lett.*, 499 (1970).

(11) E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969).

(12) Reaction mechanism involving concerted loss of two nitrogens such as shown below was ruled out because neither *cis*-9,10-dihydronaphthalene nor naphthalene was detected in the pyrolysate.



(13) H. Tanida, S. Terataki, V. Hata, and M. Watanable, *Tetrahedron Lett.*, 5341 (1969). It has been reported that in the photolysis of **11**, three products, *anti*-tricyclo[4.2.0.0^{2,5}]octane, cycloocta-1,5-diene, and *cis*-1,2-divinylcyclobutane, were obtained.

(14) E. L. Allred and A. L. Johnson, *J. Amer. Chem. Soc.*, **93**, 1301 (1971).

cyclopropyl participation in the thermolysis of azo compounds. They proposed that the orientation of cyclopropyl orbitals might play an important role on the cyclopropyl participation.

The photolysis of **1** and synthesis of monoazo compound **6** will be the subject of a future report.

Acknowledgment. I wish to thank Professors S. Masamune and D. L. Whalen for details of the "basketene" synthesis, Dr. E. Hedaya for communication of his unpublished results, Professor L. J. Winters for allowing me time to work on part of this project during my stay at Drexel, Professor C. P. Lillya for valuable discussions, and BASF for a generous gift of cyclooctatetraene.

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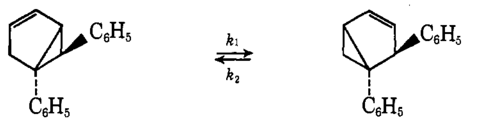
Received March 22, 1971

A Stereospecific Vinylcyclopropane Rearrangement Due to Hindered Rotation in the Biradical

Sir:

The thermal reactions of the vinylcyclopropane moiety have attracted considerable interest in recent years. The thermolysis of acyclic vinylcyclopropanes usually leads to cyclopentenes,[1] while the thermal reactions of bicyclo[3.1.0]hex-2-enes results in production of rearranged bicyclo[3.1.0]hex-2-ene(s).[2] In connection with other studies[3] we noted the facile thermal interconversion of *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene (**1**) and *trans*-4,5-diphenylbicyclo[3.1.0]hex-2-ene (**2**). Since these transformations preserved the stereochemical integrity of the phenyl groups in a formally nonconcerted process,[4] we have studied in some detail the thermal chemistry of **1** and the cis isomer **3**.



1 **2**

Thermolysis of *trans*-**1** in cyclohexane at either 130 or 170° yielded a nearly temperature-invariant mixture of 60% **1** and 40% **2** (Table I). Less than 2% of the corresponding cis isomers, **3** and **4**, could be detected in the time necessary for the **1**:**2** equilibrium to be established.

Table I. Temperature Dependence of the **1** and **2** Equilibrium[a]

Temp, °C	Starting material	Time, hr	% **1**	% **2**
130	**1**	46	59.6	40.4
130	**2**	24	59.2	40.8
170	**1**	2	59.4	40.6
170	**2**	2	58.4	41.6

[a] All products from the thermolyses were isolated by preparative vpc or tlc chromatography. Spectroscopic comparison of the isolated material with authentic samples confirmed the homogeneity and structure of the compounds.

The kinetics of the reaction were determined using a standard ampoule technique with the analysis for **1** and **2** being accomplished by vpc. The rates were calculated assuming a reversible first-order reaction, $(k_1 + k_2)t = \ln [\mathbf{1}_0 - \mathbf{1}_{\text{equil}}]/[\mathbf{1} - \mathbf{1}_{\text{equil}}]$. The reaction gave linear plots of $\ln [\mathbf{1}_0 - \mathbf{1}_{\text{equil}}]/[\mathbf{1} - \mathbf{1}_{\text{equil}}]$ *vs.* t up to the equilibrium mixture of **1** and **2** yielding $k_1 = 10^{12.6}e^{-32.4/RT}$ sec^{-1}.[5]

In contrast to the facile rearrangement of the trans compound, **1**, the corresponding cis isomer, **3**, rearranged slower and yielded besides unreacted **3** (40%), **4** (7%), **1** (32%), and **2** (21%). The rate constants for the thermolysis of **3** were obtained from the concentration *vs.* time curves by the method of Winstein, Young, and Goering[6] and yielded the following rate expression, $k_3 = 10^{13.1}e^{-36.7/RT}$.[7]

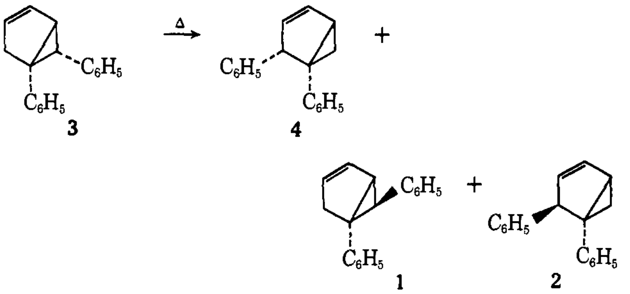


Table II. Rate of Thermolysis of *cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]hex-2-ene in Cyclohexane[a]

Temp, °C	Compd	Rate (× 10^5 sec^{-1})[b]	ΔE_{act}, kcal/mol
180.0	1	94.0	32.4
162.0	1	27.0	
144.0	1	3.9	
212.0	3	39.8	36.7
194.0	3	9.11	
180.0	3	2.56	

[a] See Table I, footnote *a*. [b] Vpc analysis was performed on a 5 ft × 1/8 in. 5% SE-30 on 100–120 mesh Varaport 30 at 135–145°. In order to obtain good precision the instrument had to be calibrated with known mixtures immediately prior to or following analysis.

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[1] (a) C. G. Overberger and A. E. Borchert, *J. Amer. Chem. Soc.*, **82**, 1007, 4891 (1960); (b) E. Vogel, *Angew. Chem.*, **72**, 4 (1960), ref 162; (c) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961); (d) H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1962); (e) H. M. Frey and D. C. Marshall, *ibid.*, **58**, 3981 (1962); (f) R. J. Ellis and H. M. Frey, *ibid.*, **60**, 4188 (1964); (g) C. S. Elliott and H. M. Frey, *ibid.*, **61**, 345 (1965); (h) H. M. Frey and A. Krantz, *J. Chem. Soc. A*, 1159 (1969); (i) R. M. Willcott and W. H. Cargle, *J. Amer. Chem. Soc.*, **89**, 723 (1967); **91**, 4310 (1969); (j) P. H. Mazzochi and H. J. Tamburin, *ibid.*, **92**, 7221 (1970).

[2] (a) W. E. von Doering and J. B. Lambert, *Tetrahedron*, **19**, 1989 (1963); (b) J. N. Lowe, *Diss. Abstr.*, **25**, 840 (1964); (c) R. H. Eastman, Final Technical Report, AFOSR Contract No. AF-49-638-1272.

[3] J. S. Swenton, A. L. Crumrine, and T. J. Walker, *J. Amer. Chem. Soc.*, **92**, 1406 (1970).

[4] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 122.

[5] Neither of the cis compounds, **3** or **4**, was detected in the kinetic determinations on *trans*-**1**. The estimated error in the rate constants is ±6%.

[6] S. Winstein, W. G. Young, and H. L. Goering, *J. Amer. Chem. Soc.*, **73**, 1958 (1951).

[7] If the integrated first-order rate expression over 4% reaction were used in determining the rate constants, apparent good plots of $\ln C_0/C$ *vs.* t result (correlation coefficients = 0.97–0.99). However, in view of the difficulty of detecting curvature in first-order plots at 0–4% reaction, the rate constants from this procedure are considered less reliable than those reported in Table II. The values obtained from the inte-