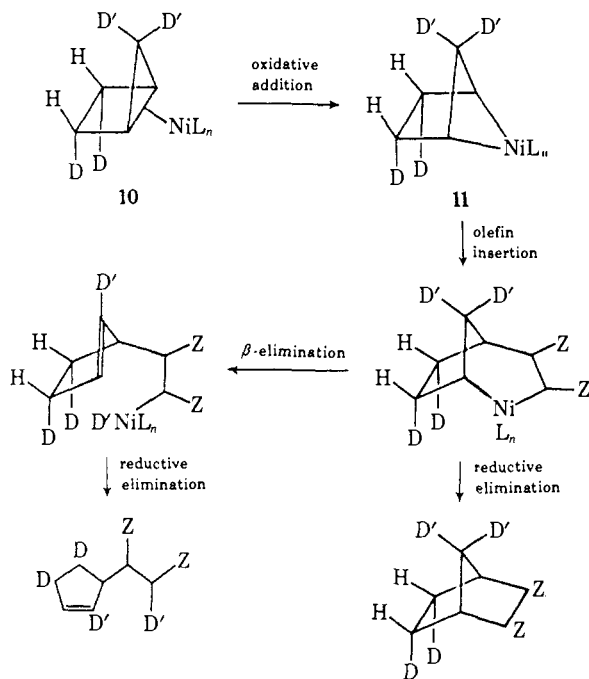


Scheme II



sense),¹⁰ and (4) the reversal of stereochemical consequence observed for the purely thermal reaction.

(10) A number of examples are given in F. D. Mango and J. H. Schachtschneider, "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971, p 223, though the mechanistic implication described therein is losing its importance.

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The Cycloreversions of Diazabicyclo[4.2.0]octenes. A Test of the Bent Bond Requirement for Concert¹

Sir:

The thermal decompositions of the diazabicyclo[4.1.0]heptenes **1a-c** to hepta-2,5-dienes are concerted cycloreversions. The facts² which support a concerted mechanism are (1) a rate of nitrogen evolution much greater than that of simple models, (2) the absence of ring-closure products (bicyclo[2.1.0]pentanes), and (3) high stereospecificity and exclusive adherence to that one of the "allowed"³ pathways which has the best overlap of the orbitals of the breaking bonds (the C₁-C₆ bridge bond and the C-N bonds). Similarly, azo compounds **2** and **3a** satisfy criteria 1 and 2 above and have been assigned a concerted mechanism of decomposition.⁴

Expansion of the cyclopropane unit of **1a-c** to a cyclobutane, as in a diazabicyclo[4.2.0]octene, should decrease the bent character⁵ of the bridge bond, weaken

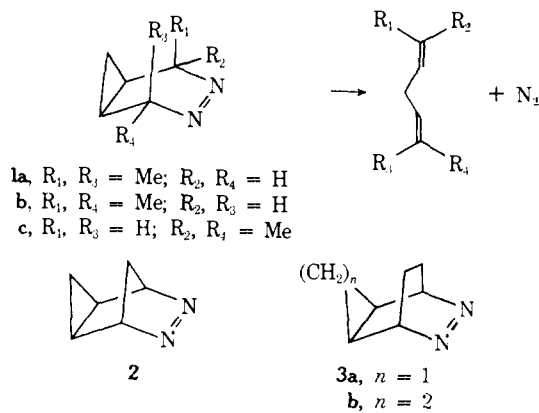
(1) This work was supported in part by a grant (GM-16962) from the National Institute of General Medical Sciences.

(2) J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **91**, 777 (1969); 92, 1086 (1970).

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

(4) E. L. Allred, J. C. Hinshaw, and A. L. Johnson, *J. Amer. Chem. Soc.*, **91**, 3382 (1969).

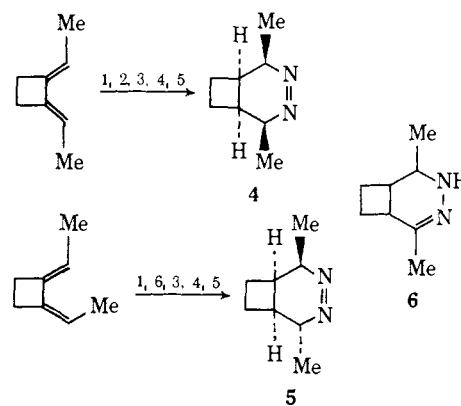
(5) (a) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949); (b) C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 2851 (1962); 3161 (1963); (c) Cf. also A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).



the overlap with the two breaking C-N bond orbitals in the concerted transition state, and thereby narrow not only the energy gap between the concerted paths but also that between the concerted and non-concerted ones. That the borderline with a non-concerted process may have been reached in a cyclobutane derivative is suggested by the behavior of **3b**, which decomposes much more slowly than does its cyclopropane analog **3a** and is reported to form ring-closure products.⁶

Two compounds appropriate for the application of all three criteria to a test of the bent bond requirement are *syn,cis*- and *trans*-2,5-dimethyl-3,4-diazabicyclo[4.2.0]oct-3-ene (**4** and **5**). Syntheses of **4** and **5** are accomplished by the highly stereospecific routes shown in Scheme I. The *syn, cis* configuration of **4** is con-

Scheme I



firmed by conversion of its precursor **7** to the urazole **8**,⁸ which in turn is obtained from the known⁹ cyclooctatriene-*N*-phenyltriazolinedione adduct **9** by ozonolysis of the unsaturated bridge and reduction in several steps.

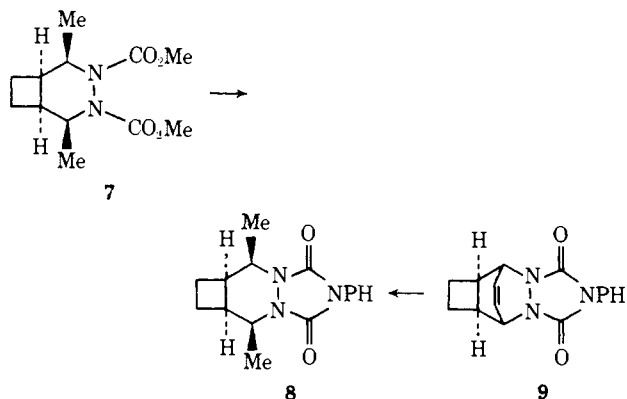
Although heating *cis* azo compound **4** in diphenyl

(6) (a) E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1971); *Tetrahedron Lett.*, 387 (1972).

(7) Notes to Scheme I: (1) bisethylidene cyclobutane isomers prepared by the method of P. Heimbach and R. Schimpf, *Angew. Chem., Int. Ed. Engl.*, **8**, 206 (1969); (2) dimethyl azodicarboxylate; (3) H₂/Pt; (4) KOH-H₂O, then H⁺, all with rigorous exclusion of air; (5) vacuum line isolation of the volatile crystalline hydrazine followed by treatment of a benzene solution with oxygen; (6) *N*-methyltriazoline-3,5-dione. Compounds **4** and **5** show λ_{max} 395 nm, ε 150, and λ_{max} 392 nm, respectively, in ether. The nmr spectra are appropriate for the assigned structures. Both tautomerize irreversibly with extreme ease to the hydrazone **6**.

(8) E. W. Petrillo, Jr., Ph.D. Dissertation, Yale University, 1973.

(9) (a) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967); (b) D. G. Farnum and J. P. Snyder, *Tetrahedron Lett.*, 3861 (1965).



ether solution causes quantitative conversion to the hydrazone **6**, injection of a benzene solution of **4** into a hot (200°) evacuated Pyrex chamber and collection of the products in a trap at -196° give a mixture of 60% of hydrazone **6** and 40% of pure *cis,cis*-octa-2,6-diene (**10**). Similarly, the trans azo compound **5** gives pure *cis,trans*-octa-2,6-diene (**11**) as the hydrocarbon product. The potential ring-closure products, the dimethylbicyclo[2.2.0]hexanes **13**, **14**, or **15**, are not observed. Moreover, control experiments (Table I) show that neither any of the hydrocarbons **13**–**15**

Table I. Per Cent Yields^a of C₈H₁₄ Hydrocarbons in the Vapor-Phase Pyrolysis of **4** and **5**

Reactant	Products					
	10	11	12	13	14	15
4 ^b	>99	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
5 ^b	<i>f</i>	>99	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
6 ^b	0.6 ^c	0	0	0	0	0
13 ^{c,d,h}	0	63	1.2	0	0	35.8
14 ^{c,h}	8	0	92	0	0	<i>e</i>

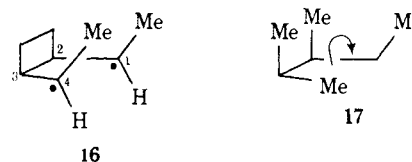
^a Yield relative to total of volatile products as determined by electronically integrated vpc analysis using 20 ft × 1/8 in. γ-methyl-γ-nitropimelonitrile column. ^b Chamber pyrolysis (120 sec at 200°). ^c Pyrolysis at 197.4° in sealed capillary tubes. ^d *t*_{1/2} = 10,000 sec; pyrolysis for 2.5 half-lives. ^e **14** and *dl*-3,4-dimethylhexa-1,4-diene not resolved by vpc. Yields do not include any of the latter formed. ^f Less than 0.1%. ^g Yield estimated by comparison to the trace peak relative to amount of **13** formed in pyrolysis of **4**. ^h Compare W. R. Roth, personal communication, as cited by R. G. Bergman in "Free Radicals," Vol. I, J. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, p 229. We are indebted to Professor Roth for a reference spectrum of **13**. Compound **14** was synthesized independently (ref 8).

nor the hydrazone **6** is an intermediate in the formation of the dienes. The stereospecificities **4** → **10** and **5** → **11** are each >99.9%.

Azo compounds **4** and **5** of the cyclobutane series lose nitrogen at rates (*t*_{1/2} ~ 70 sec at 200°) about five times those of Allred's compound **3b**⁶ but much slower than the cyclopropane analogs **1a**–**c** (*t*_{1/2} ~ 30 min at -10°).² The rate decrease may result from less bent character in the bridge bond. Although the stereospecificity for **4** and **5** also should decline relative to that for **1a**–**c**, it remains higher than the upper limit of our analysis.

An interpretation of the results for **4** and **5** in terms of a 1,4-diradical intermediate would require that the

intermediate be formed specifically in conformation **16** and that cleavage of the bridge bond (C₂–C₃) in **16** be at least 1000 times faster than stereorandomizing bond rotations. There are good reasons to believe¹⁰ that there would be no significant rotational barriers introduced by conjugation of the 1,4 orbitals with the cyclobutane ring orbitals of **16**. In the absence of such special effects, rotational barriers about C_α–C_β bonds in hydrocarbon radicals may be estimated to be not more than about one-sixth of those in the corresponding hydrocarbons.¹¹ The barrier for the rotation shown in the model hydrocarbon 2,3-dimethylpentane **17** is 7



kcal/mol,¹⁴ from which it may be estimated that the barrier to rotation about the C₁–C₂ bond of **16** would be ≤1.2 kcal/mol. The 1000-fold stereospecificity of diene formation at 200° corresponds to ΔΔ*F*[‡] ≥ 6.5 kcal/mol, which thus would require that C₂–C₃ bond cleavage in the hypothetical diradical **16** have a *negative* activation energy. It is conceivable that "through-bond" coupling might increase the rotational barrier,¹⁵ but the peculiar requirements that the diradical be formed exclusively in conformation **16** and that it fail to cyclize to 2,3-dimethylbicyclo[2.2.0]hexanes¹⁶ would remain. We therefore interpret the decompositions of **4** and **5** as concerted reactions.

(10) R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971).

(11) (a) The following values (in kcal/mol) are illustrative: propane (2.8), propyl radical (0.4–0.5); isobutane (3.6), isobutyl radical (0.3).^{12,13}

(12) H. E. O'Neal and S. W. Benson in "Free Radicals," Vol. II, J. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, Chapter 17, and references cited therein.

(13) H. Fischer, ref 12, p 483 and references cited therein.

(14) U. Zirnits and M. M. Sushchinskii, *Opt. Spectrosc. (USSR)*, **16**, 489 (1964), as cited in ref 12.

(15) L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, **94**, 4599 (1972).

(16) The pyrolysis of 5,6-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene gives substantial quantities of **13** and **15**: W. R. Roth and M. Martin, *Tetrahedron Lett.*, 3865 (1967).

(17) National Science Foundation Graduate Fellow, 1969–1972; National Science Foundation Trainee, 1972–1973.

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Chemical Consequences of Strong Hydrogen Bonding in the Reactions of Organic Ions in the Gas Phase. Base Induced Elimination Reactions

Sir:

The strong hydrogen bond, formed by the binding of two n-donor bases to a labile proton, is an important structural moiety which warrants consideration in a variety of gas-phase ion-molecule reactions. Bimolecular¹ processes in which strong hydrogen bonding has been observed to play an important role include

(1) For a discussion of intramolecular interactions of remote functional groups in which strong hydrogen bonding is important, see T. H. Morton and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **94**, 1369 (1972).