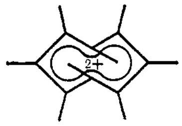
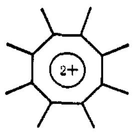
Another structure for this ion which deserved consideration was that of the octamethylcyclooctatrienyl dication **6** which could conceivably exist in two forms, **a** or **b**, as shown below. In **b** one would conclude that the methyl groups should be equivalent. We cannot rigorously exclude **a**, but this structure seems unlikely.

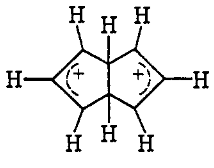


6a



6b

We also considered the possibility that cyclooctatetraene might rearrange to the bicyclo[3.3.0]octadienyl dication (**7**) in the super acid medium $HFSO_3$–SbF_5.[6] This was not the case, for when cyclooctatetraene was added to 1 : 1 fluorosulfuric acid–antimony pentafluoride in sulfur dioxide solution, a poorly resolved spectrum of the homotropylium ion was obtained.[7] It was possible to prepare a solution of this ion giving a well-resolved spectra by adding cyclooctatetraene to fluorosulfuric acid in sulfur dioxide and then adding antimony pentafluoride. Aside from slight changes in chemical shifts, the spectrum was identical with that reported for the homotropylium cation. We are continuing our studies on pentalenyl dications and bicyclo[3.3.0.]octadienyl-dications.



7

Acknowledgment. The National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society are thanked for partial support and the Badische Anilin und Soda Fabrik for a gift of cyclooctatetraene.

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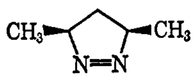
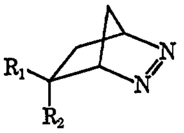
Thermolysis of *exo*-6,7-Diazatricyclo[3.2.1.0^{2,4}]-6-octene

Sir:

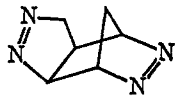
It is well established that simple alkyl cyclic azo compounds such as **1** and **2** thermally decompose in a stepwise manner by extrusion of molecular nitrogen to give 1,3-diradical-like intermediates which then form products.[1,2] As we reported recently,[3] **3** decomposes with an appreciable contribution from a reverse Diels–Alder reaction pathway which does not involve nitrogen loss. We now wish to record evidence that *exo*-6,7-diazatricyclo[3.2.1.0^{2,4}]-6-octene (**4**) decomposes by yet another mechanism. In this connection, **4** *shows an enormous reactivity ratio of* 10^{11} compared to structurally related **2**.



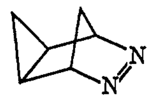
1



2a, $R_1 = H; R_2 = H$
b, $R_1 = OCH_3; R_2 = H$
c, $R_1 = H; R_2 = OCH_3$



3

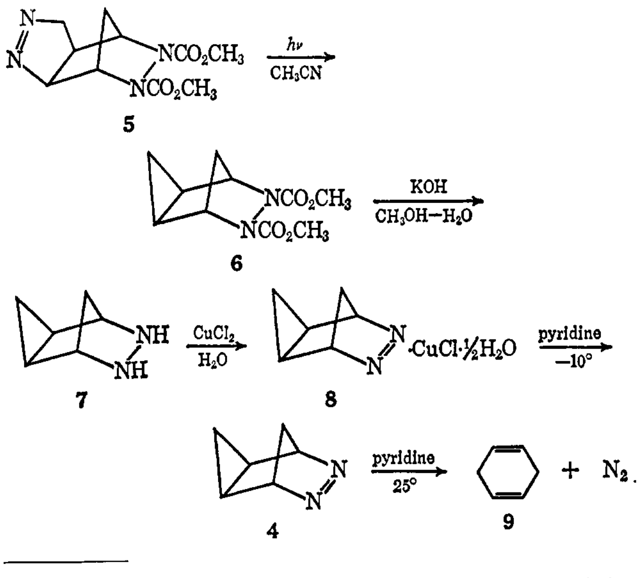


4

Scheme I outlines the synthetic sequence used to convert **5**[4] to **4**.[5] Irradiation of **5** in acetonitrile solution with 3500-Å light for 48 hr produced **6** in near-quantitative yield: mp 84–86° (from dichloromethane–pentane after column chromatography on Florisil); $\lambda_{max}^{CCl_4}$ 3.30 μ (cyclopropyl); nmr, τ_{CDCl_3} 9.59 (2 H, multiplet), 8.72 (4 H, multiplet), 6.33 (6 H, singlet), and 5.46 (2 H, broad singlet). The assignment of the *exo* configuration to **6** follows from the known structure of **5** with its *exo* locked-C_3 carbon.[4]

Hydrolysis–decarboxylation of **6** with hot potassium hydroxide in aqueous methanol led to hydrazine **7**. Exposure of this compound to air or mercuric oxide resulted in immediate oxidation with the accompanying formation of nitrogen and 1,4-cyclohexadiene (**9**). Treatment of **7** with cupric chloride in water gave the brick red cuprous chloride complex **8**:[5] 56% (from **6**); decomposes slowly at ~100°; λ_{max}^{KBr} 6.74 μ (–N=N–);[4] $\lambda_{max}^{CH_3CN}$ 348 mμ (ϵ ~200).[4] Azo compound **4** was liberated by dissolving **8** in pyridine at temperatures <−10°. The nmr spectrum of the solution showed

Scheme I



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(1) R. J. Crawford and B. H. Al-Sader, *Can. J. Chem.*, **46**, 3301 (1968); R. J. Crawford and D. M. Cameron, *ibid.*, **45**, 691 (1967); R. J. Crawford and G. L. Erickson, *J. Amer. Chem. Soc.*, **89**, 3907 (1967); R. J. Crawford and L. H. Ali, *ibid.*, **89**, 3908 (1967); R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); and other papers in the series.

(2) E. L. Allred and R. L. Smith, *ibid.*, **89**, 7133 (1967).

(3) J. C. Hinshaw and E. L. Allred, *Chem. Commun.*, 72 (1969).

(4) The synthesis and characterization of **5** have been reported elsewhere: E. L. Allred and J. C. Hinshaw, *J. Amer. Chem. Soc.*, **90**, 6885 (1968).

(5) Satisfactory elemental analyses were obtained for **6** and **8**.

complex overlapping multiplets centered near τ 10.1 (2 H) and 9.6 (4 H) and a broad singlet at τ 5.40 (2 H). The very high field signals for six protons are just what is expected for **4**. Upon warming the solution to room temperature the signals for **4** disappeared and 1,4-cyclohexadiene (**9**) signals appeared at τ 7.8 and 4.7.

Thermolysis of **4** in pyridine solvent at 25° produced a quantitative yield of nitrogen. Glpc analysis (20% SE-30 on Chromosorb W column) of the reaction solution showed **9** as the only detectable product.[6] Analysis with methylcyclohexane present as an internal standard established that **9** was formed quantitatively (>99%).

The first-order rate constants for decomposition of **4** in pyridine were determined at nine temperatures over the range −5 to +11° by periodic integration of the increasing τ 7.8 protons of **9** against the protons of acetonitrile internal standard. Some kinetic results are given in Table I along with pertinent comparisons to **1**[1] and **2a**.[7]

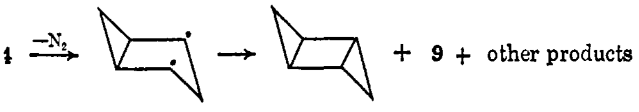
Table I. Thermolysis Rate Data for Some Azo Compounds

Compd	Temp, °C	10^4k, sec^{-1}	Rel rate	E_a, kcal/mole
4[a]	−3.5	0.77[b]	1.6×10^{11}	18.9 ± 1.5[c]
4[a]	+5.5	2.44[b]		
2a	−3.5		1.0[d]	37.3 ± 0.3
1[e]	−3.5		0.01[d]	40.3 ± 0.3

[a] About 0.2 *M* in **4**. [b] Calculated from 25–30 integrations covering the range 0 to *ca.* 80% reaction. [c] Based on an Arrhenius plot of nine rate constants over the temperature range of −5 to +11°. The uncertainty is root-mean-square deviation. [d] Estimation based on gas-phase results and extrapolation to −3.5° from other reported data.[1,7] [e] *cis* isomer.

On the basis of the structural similarity between **4** and system **2**, a possible mechanistic process for the thermolysis of **4** is outlined in Scheme II.[2] If **4** reacts *via* a 1,3-diradical intermediate(s) one expects at least some ring closure with a great propensity for inversion of configuration to give *trans*-tricyclo[3.1.0.0^{2,4}]hexane (**10**).[2,8] On the contrary, 1,4-cyclohexadiene (**9**) is the only product observed. Our analytical method would have detected the presence of <0.1% **10**.[4,6] Control experiments showed that **10** and the other C_6H_8 hydrocarbons are completely stable under the thermolysis conditions. The extremely high product specificity from **4** strongly suggests that **4** and **2** decompose by different mechanisms.

Scheme II

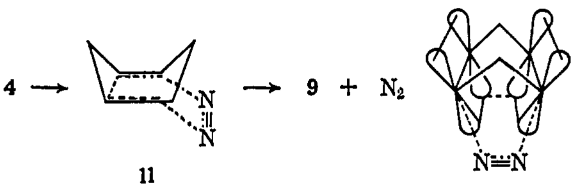


10

The exceptionally high reactivity of **4** also is not consistent with the decomposition of **4** by Scheme II. A reactivity ratio of 10^{11} is many orders of magnitude greater than it should be if **4** and **2** decompose by similar mechanisms. For instance, the reactivity ratio for **2a**, **2b**, and **2c** is only 1.0:6.0:0.9.[2]

A more plausible mechanism which accounts for the results involves synchronous nitrogen elimination and 1,4-cyclohexadiene (**9**) formation as illustrated by Scheme III. Such a concerted route is an orbital-symmetry-allowed process.[9] The cyclopropane bonding orbitals in **4** are especially favorably oriented for overlap with the developing orbitals at C_1 and C_5 in the transition state for nitrogen departure (see end-view **11**). In this regard, Berson and Olin[10] have reported an interesting stereochemical study of the thermolysis of the 3,4-diazabicyclo[4.1.0]heptyl system which shows a strong preference for a transition state of similar geometry. It is noteworthy that the spatial orientation of the cyclopropyl ring in **4** is comparable to the favored relationship found in other kinds of reactions which show marked rate enhancement due to cyclopropyl participation.[11,12]

Scheme III



11

11, end view

In addition to the electronic factor, relief of steric interaction between C_3 and C_8 hydrogen atoms and the additional strain imposed by the cyclopropyl ring undoubtedly make some contribution to the enormous 10^{11} rate acceleration found with **4**. At present there is not sufficient information for making a separation of the three effects. We have experiments under way which are aimed at estimating how much is due to each factor.

Acknowledgments. We express appreciation to the National Science Foundation for support of this work with Grant GP-6923. We thank the National Institutes of Health for purchase of a gas chromatograph through Biomedical Sciences Support Grant No. 1805FR07092-01.

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(6) With our analytical conditions all C_6H_8 hydrocarbons such as tricyclo[3.1.0.0^{2,4}]hexane (**10**),[4] bicyclo[3.1.0]hexene, 1,3-cyclohexadiene, etc., were readily detectable.

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(11) K. B. Wiberg, V. Z. Williams, and L. E. Friedrich, *ibid.*, **90** 5338 (1968).

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(13) NDEA Title IV Fellow, 1968–70.

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A Pure Intramolecular Charge-Transfer Transition. Substituted N-Alkyl-N-nitrosoanilines[1]

Sir:

While intramolecular charge-transfer bands in absorption spectra have been postulated for some time,[2]

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(1) This investigation was supported in part by National Science Foundation Grant GP7551, which we gratefully acknowledge.

(2) J. N. Murrell, *Quart. Rev.* (London), **15**, 191 (1961).