Thermal and Photodecomposition Studies with the *exo*- and *endo*-5-Methoxy-2,3-diazabicyclo[2.2.1]hept-2-ene System

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Abstract: Decomposition of the *exo* and *endo* epimers of 5-methoxy-2,3-diazabicyclo[2.2.1]hept-2-ene (Ix and In, respectively) by either heat or light leads to product which consists almost entirely of the *cis* and *trans* isomers of 2-methoxybicyclo[2.1.0]pentane (*cis*-III and *trans*-III, respectively). The two azo epimers give widely different *cis*:*trans* product ratios by gas phase thermolysis. Similarly, direct photolysis in the liquid phase gives a different product ratio for each epimer. It is of particular interest that in both of these decompositions each epimer produces product which shows a net crossover of configuration, *i.e.*, excess *trans*-III from Ix and excess *cis*-III from In. Benzophenone-sensitized photolysis leads to the same product ratio for each epimer. In contrast, direct photolysis of crystalline Ix and In affords product with highly retained structure for each epimer. All of the observations can be explained readily on the basis of a mechanistic scheme involving interconverting pyramidal diradicallike intermediates which are short-lived. To account for the cases of product crossing over, it is proposed that structurally inverted diradicals arise directly upon nitrogen elimination from Ix and In and that closure occurs before the intermediates fully equilibrate. This inversion is thought to be a consequence of recoil from C–N bond breaking. Significant differences in product ratios from thermolysis, direct photolysis, and sensitized photolysis provide evidence that ground-state singlet diradicals, electronically excited singlet diradicals, and electronically excited triplet diradicals are involved, respectively.

At the present time thermal and photoinduced decompositions of azo compounds are receiving intensive study.[1–13] Some of these investigations are of special interest because of the importance of the results in several directions. Since azo compounds decompose *via* free-radical intermediates, study of radical coupling is instructive about molecular and mechanistic processes too fast for normal measurement. Among these processes are conformational changes at radical centers,[2b,3a,b] intramolecular σ-bond rotations,[1b,4–7a] and the inversion of electron spin.[1,5,7a,8] Investigation of the photochemistry of azo compounds promises to provide fundamental and useful information about the chemistry of excited states.[1,5,7–10] The possibility of producing an intermediate radical pair appropriate for comparing the chemistry of a vibrationally excited ground state with electronically excited states is intriguing. In another aspect, decomposition of cyclic azo structures is of great value for the synthesis of highly strained compounds.[1a,2a,d]

Scrutiny of the literature suggests that cyclic azo compounds will afford the most information concerning the above mechanistic points. In view of the evidence that 1-pyrazolines decompose thermally by way of nitrogen-free intermediates which are best described as 1,3-diradicals,[4] we undertook a study to ascertain the behavior of such intermediates generated by a variety of means. The compounds chosen for the initial investigation were *exo*- and *endo*-5-methoxy-2,3-diazabicyclo[2.2.1]hept-2-ene, Ix and In, respectively. Since conrotatory coupling[4] and σ-bond rotations are prohibited for the intermediates from this system, it was anticipated that the interpretation of results would be less ambiguous than for monocyclic cases.

We previously reported the thermolysis results in preliminary form.[2b] This paper amplifies the earlier report, presents the results of our photolysis investigation, and discusses the mechanistic implications.

Results

Synthesis of Ix and In. Azo compounds Ix and In were prepared from the corresponding 2,3-dicarbomethoxy-2,3-diazabicyclo[2.2.1]heptan-5-ol of established 5-*exo* and 5-*endo* configuration.[14] Treatment of the *exo*-alcohol with sodium hydride and methyl iodide in tetrahydrofuran gave 2,3-dicarbomethoxy-*exo*-5-methoxy-2,3-diazabicyclo[2.2.1]heptane. Reaction of the methoxy derivative with methanolic potassium hydroxide[15] afforded *exo*-5-methoxy-2,3-diazabicyclo-[2.2.1]heptane. Mercuric oxide oxidation[16] readily

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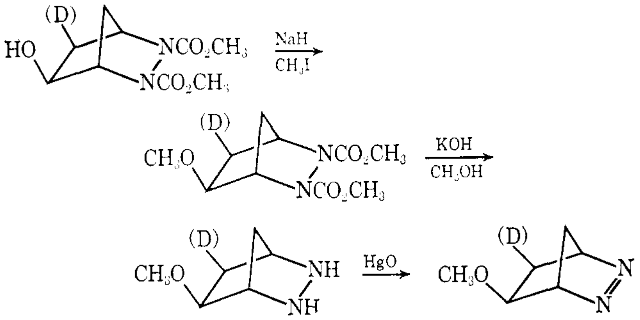
transformed this hydrazine to Ix. The alcohol of *endo* configuration[14] was converted to In with an analogous reaction sequence. Spectroscopic properties (Experimental Section) are entirely consistent with the assigned azo structures. Distinctly different nmr and infrared spectra indicate that no loss of C_5 configuration occurred in the preparation of either Ix or In. As expected, the C_5 proton signal of Ix is found upfield (0.93 ppm) from the corresponding signal of In.[14,17] Deuterium labeled *exo*-6-*d*-Ix was obtained from 2,3-dicarbomethoxy-*exo*-2,3-diazabicyclo[2.2.1]heptan-5-ol which had been labeled specifically in the *exo*-6 position.[18]

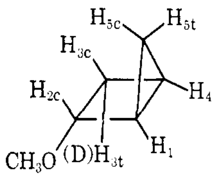


Ix

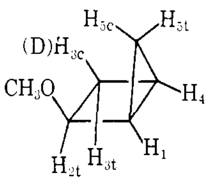
Structural Elucidation of Products. Decomposition of Ix and In by either heat or light led to product which consisted of two major components (total yield >90%) as indicated by vpc analysis with a variety of columns. In the nmr spectrum of the product mixture there are absorptions above τ 9.1 characteristic of cyclopropyl protons, two methoxyl group absorptions at τ 6.85 and 6.72, and the absence of protons below τ 6.1. It follows from the presence of high-field protons and the lack of vinyl protons that the compounds are the epimers of 2-methoxybicyclo[2.2.1]pentane. Elemental analysis of the mixture is in complete accord with this.

The isomers were separated by preparative vpc with a tetraethylene glycol column for the work of assignment of configuration. The early and late eluting compounds were assigned the structures of *trans*-III and *cis*-III, respectively, on the basis of a number of lines of evidence.

Several features of the proton nmr spectra provide criteria for assignment of configuration. The C_2 proton signal of each isomer is shifted downfield from the other proton signals by the methoxyl substituent and is readily recognizable. Models show clearly that the C_2 proton of *trans*-III lies above and in a shielding region of the cyclopropane ring, while the corresponding proton of *cis*-III is oriented away from the ring. On this basis the C_2 proton signal is expected to occur at a higher field for *trans*-III than for *cis*-III.[19] This prediction assigns the *trans*-III structure to the early eluting isomer since it has the C_2 proton signal at 0.50 ppm higher field. Chemical shift observations for the known epimeric 2-methoxybicyclo[3.1.0]hexanes with similarly oriented C_2 protons are completely consistent with this assignment. Freeman[20] observed that the C_2 proton signal of the *trans* isomer occurred at 0.37 ppm higher field than for the *cis* isomer.



trans-III



cis-III

Each of the methylene cyclopropyl protons of *cis*-III and *trans*-III occurs as a separate complex multiplet above τ 9.1 and is readily identifiable as H_{5c} or H_{5t} on the basis of the width at half-heighth (w_h).[21] One expects a deshielding effect upon H_{5c} by a *cis*-2-methoxyl substituent on the bicyclopentane ring which is similar to the effect of the 5-*exo*-hydroxyl[17] and 5-*exo*-chloro[22] groups on the *anti*-C_7 proton in the 2-norbornene system. This situation prevails with the above assignments for *cis*-III and *trans*-III. The late eluting isomer has the H_{5c} signal downfield *ca.* 0.3 ppm from the corresponding resonances of the other component and unsubstituted bicyclo[2.1.0]pentane.[3a] The same deshielding effect has been reported for the *cis*- and *trans*-2-methoxybicyclo[3.1.0]hexanes[20] and for other fused ring systems having a hydroxyl group on a carbon α to a cyclopropane ring.[23]

Long-range proton coupling across four bonds is a valuable diagnostic tool for assignment of configuration in rigid bicyclic systems because of its stereospecifity.[17,22] In this regard, protons H_{3t} and H_{5t} have the required "transoid" or "W" relationship[17,22,24] to one another while H_{3c} and H_{5c} or H_{3c} and H_{5t} do not. Thus with appropriate deuterium labeling at C_3 it should be possible to distinguish between the *cis*-III and *trans*-III structures. Decomposition of *exo*-6-*d*-Ix provided the epimers of III which have the necessary *cis* relationship between the methoxyl group and C_3 deuterium atom.[25] The results are in accord with expectations. Deuterium labeling greatly simplifies the H_{5t} pattern of the early eluting compound but leaves the same signal of the other isomer unchanged.[26] This clearly indicates that the deuteron and methoxyl group for the first case are *trans* to C_5.

Since thermal equilibration of *cis*-III and *trans*-III indicated that, surprisingly, *cis*-III is more stable than *trans*-III (*vide infra*), we felt that additional confirmation for the configurational assignments was desirable.

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[19] Long-range shielding by a cyclopropane ring is well established: (a) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963); (b) R. S. Boikess and S. Winstein, *ibid.*, **85**, 343 (1963); G. L. Closs and H. B. Klinger, *ibid.*, **87**, 3265 (1965); C. U. Pittman and G. A. Olah, *ibid.*, **87**, 5123 (1965).

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[21] Vicinal *cis* protons have been observed to have substantially larger coupling constants than vicinal *trans* or geminal protons in cyclopropane systems.[19a] Proton H_{5t} is *cis* to H_1 and H_4 and thus will have a much larger w_h than H_{5c}. The values are 17–19 cps for H_{5t} and 7 cps for H_{5c}.

[22] P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

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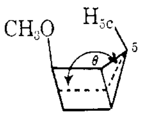
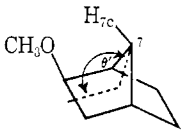
[25] There was no indication that deuterium scrambling occurred as a consequence of decomposition. The nmr spectrum of the early eluting component showed the disappearance of one proton in the complex absorption centered near τ 8.2. For the other isomer, one proton near τ 8.8 vanished.

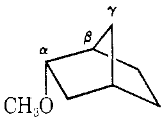
[26] A comparison of w_h for H_{5t} of deuterated and nondeuterated *trans*-III suggests that the long-range coupling is of the order of 1–2 cps. The value reported for bicyclo[2.1.0]pentane is 1.2 cps.[3a]

In this connection, recent studies show that ^{13}C magnetic resonance spectroscopy provides information regarding conformational and configurational assignments.[27,28] It is particularly noteworthy that the signals of carbons γ to axial methyl groups on cyclohexyl rings are shifted far upfield (>5 ppm) from the signals of carbons γ to equatorial methyl groups or the carbons of cyclohexane.[27] This indicates the ^{13}C chemical shift differences caused by γ substituents will be helpful in establishing configurations in fused small ring systems.

A comparison of ^{13}C magnetic resonance spectra revealed that the C_5 signal of the late eluting compound appears at 4.88 and 5.51 ppm higher field than the corresponding signal of the other isomer and bicyclo[2.1.0]pentane, respectively. In order to see if this observation is characteristic of such structural arrangements, we examined the C_7 chemical shifts for *exo*- and *endo*-2-methoxynorbornane and for the Ix–In systems.[29] The C_7 signal of *exo*-2-methoxynorbornane occurred at 2.68 ppm higher field than for the *endo* isomer; the Ix C_7 signal was 1.82 ppm upfield from the same signal of In. These substantial upfield shifts are attributable to steric interaction between a γ-*cis*-methoxyl group and the H_{5c} (or H_{7c}) proton. It has been proposed that such shifts are due to induced polarization of charge along the H–^{13}C bond.[27] The difference in magnitude of upfield shift found for the bicyclopentane and norbornane systems is qualitatively consistent with a steric effect explanation because of the difference in geometry. The dihedral angle between the planes of the two rings for bicyclopentane (θ) is 109°[30] whereas the angle between the $C_1C_2C_3C_4$ and $C_1C_7C_4$ planes of norbornane (θ') is 123.5–126°.[31] This difference will cause the bicyclopentane *cis*-2-methoxyl group and H_{5c} proton to be in closer proximity than the *exo*-2-methoxyl group and H_{7c} proton of the norbornane.







The ^{13}C chemical shift correlation assigns the *cis*-III structure to the late eluting product in complete agreement with the conclusions based on the proton nmr studies.

Another entirely different kind of evidence for configurational assignment comes from the mechanistic studies of heat- and light-induced decomposition. When Ix or In is decomposed thermally in the gas phase or photolytically in the liquid phase, the product shows net inversion of configuration from each isomer based on the foregoing assignments, *i.e.*, excess *trans*-III from Ix and excess *cis*-III from In (Tables II and III). In striking contrast, photodecomposition of solid phase Ix or In gives product with highly retained structure in each case (Table III). These results are explained readily on mechanistic grounds (*vide infra*) if the structures are as assigned, but they present a mechanistic dilemma if the assignments are reversed.

Thermolysis. Table I shows some kinetic results for the thermolysis of Ix and In, along with pertinent data for comparison of reactivity with 2,3-diazabicyclo[2.2.1]hept-2-ene (IV). The experiments with Ix and In were carried out in evacuated Pyrex tubes which had been sealed under nitrogen. For each rate determination decomposition was followed by vpc to *ca.* 80% completion by periodically measuring the development of combined III against an internal standard of 1,2-dimethoxyethane. Both isomers exhibited good first-order kinetics.

Table I. Kinetics of the Thermolysis of Ix and In at 160.0 ± 0.05°

Compd	10^4k, sec^{-1}	Relative rate
IV	1.10[a]	1.0
Ix	5.4[b]	4.9
In	0.80[b]	0.7

[a] Calculated from other reported data.[16] [b] Development of combined III measured against an internal standard of 1,2-dimethoxyethane with a 5-ft 15% Carbowax 20M vpc column.

Results of the product composition studies for gas-phase thermolysis of Ix and In are summarized in Table II. Decompositions were carried out with samples of azo compound which had been degassed and sealed under nitrogen in evacuated Pyrex tubes. Upon completion of reaction at 135° the total internal pressure approximated 100 mm. Under these reaction conditions *cis*-III and *trans*-III were the only products (>95% yield). The product ratios were found to be independent of pressure over the range of 10–100 mm. Decomposition of *exo*-6-*d*-Ix did not lead to scrambling of the deuterium label.[25]

Table II. Thermal Decomposition of Ix and In and Isomerization of Products *cis*-III and *trans*-III[a]

Compd	Temp, °C	% composition[b] *cis*-III	% composition[b] *trans*-III
Ix	135[c]	63.0 ± 0.6	37.0 ± 0.6
Ix	198.9[d]	85.6 ± 0.4	14.4 ± 0.4
Ix	220.0[e]	85.5 ± 0.4	14.5 ± 0.4
In	135[f]	93.6 ± 0.5	6.4 ± 0.5
In	198.9[d]	85.9 ± 0.5	14.1 ± 0.5
In	220.0[e]	85.2 ± 0.5	14.8 ± 0.4
47.9% *cis*-III + 52.1% *trans*-III	135[g]	48.9 ± 0.3[h]	51.1 ± 0.3[h]
47.9% *cis*-III + 52.1% *trans*-III	198.9[d]	85.4 ± 0.5	14.6 ± 0.5

[a] Carried out in sealed 25-ml Pyrex tubes. [b] Determined with a 20-ft 15% tetraethylene glycol on Chromosorb P vpc column. [c] For 30 hr (*ca.* 5 half-lives). [d] For 16 hr. [e] For 5.5 hr. [f] For 100 hr (*ca.* 2.5 half-lives). [g] For 100 hr. [h] Equilibrium composition at 135° is 87.1% *cis*-III and 12.9% *trans*-III as extrapolated from the equilibrium constant data at 198.9 and 220°.

Product interconversion was examined under decomposition conditions and at higher temperatures with the aid of a 47.9:52.1 *cis*-III:*trans*-III mixture obtained

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(29) The full details of this investigation will be presented in a subsequent paper.

(30) Y. H. Tai and R. K. Bohn, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1–5, 1968, paper P-99. The above angle is the revised value reported at the meeting; private communication from Professor R. K. Bohn.

(31) Range for θ' based on the data of Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Chem. Soc. Jap.*, **40**, 1552 (1967), and J. F. Chiang, C. F. Wilcox, and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968).

Table III. Direct Photolysis of Ix and In[a]

Compd	Solvent or or state	Quenching agent (concn, *M*)	% composition[b,c] *cis*-III	*trans*-III
Ix	Pentane[d,e]		45	55
Ix	Pentane[d,e]	Piperylene (0.3)	42	58
Ix	Crystalline[f]		97	3
In	Pentane[d,e]		84	16
In	Pentane[d,e]	Piperylene (0.3)	84	16
In	Crystalline[f]		35	65
In	Glassy[f,g]		64	36
45% *cis*-III + 55% *trans*-III[h]	Pentane		46	54
84% *cis*-III + 16% *trans*-III[h]	Pentane		85	15

[a] Hanovia Type S 200-W lamp with Pyrex filter. [b] Determined with a 20-ft 15% tetraethylene glycol Chromosorb P gas chromatography column. [c] Reproducibility of experiments *ca.* ±2%. [d] 0.01 *M* azo compound. [e] For 24 hr at room temperature. [f] Neat, for 15 hr at −80°. [g] See ref 32. [h] For 58 hr at room temperature.

Table IV. Sensitized Photolysis of Ix and In

Compd (concn, *M*)	Solvent	Sensitizer (concn, *M*)	Quencher (concn, *M*)	— % composition[a] — *cis*-III	*trans*-III
Ix (0.01)[b,c]	Cyclohexane			47	53
Ix (0.005)[c,d]	Cyclohexane	Triphenylene (0.009)		73	27
Ix (0.005)[c,d]	Cyclohexane	Triphenylene (0.009)	Piperylene (0.1)	44	56
Ix (0.02)[c]	Cyclohexane	Benzophenone (0.4)		78	22
Ix (0.01)[c,d]	Cyclohexane	Benzophenone (0.05)		76	24
Ix (0.01)[c,d,f]	Cyclohexane	Benzophenone (0.05)	Piperylene (0.1)	77	23
Ix (0.01)[e]	Pentane	Pyrene (0.05)		48	52
In (0.01)[b,c]	Cyclohexane			82	18
In (0.005)[c,d]	Cyclohexane	Triphenylene (0.009)		78	22
In (0.005)[c,d]	Cyclohexane	Triphenylene (0.009)	Piperylene (0.1)	80	20
In (0.02)[c]	Cyclohexane	Benzophenone (0.4)		79	21
In (0.01)[c,d]	Cyclohexane	Benzophenone (0.05)		76	24
In (0.01)[c,d,f]	Cyclohexane	Benzophenone (0.05)	Piperylene (0.1)	78	22
In (0.01)[e]	Pentane	Pyrene (0.05)		85	15
47% *cis*-III + 53% *trans*-III[c,g]	Cyclohexane	Triphenylene (0.009)		47	53

[a] Reproducibility of experiments *ca.* ±2%. [b] <10% conversion to products. [c] At 2537 Å. [d] Experiments with and without piperylene were carried out simultaneously, under identical conditions, using a merry-go-round assembly in a Rayonet photochemical reactor. [e] Hanovia Type S lamp with Pyrex filter. [f] Piperylene reduced total product formation by a factor of *ca.* 4.3. [g] Exceeded time necessary for 100% conversion to products.

from photolysis of neat Ix. As shown in Table II isomerization is barely detectable at 135° after 100 hr. However, product interconversion is rapid at temperatures near 200°. The above mixture produces the same equilibrium composition at 198.9° as the decomposition of Ix or In at this temperature. Using the average equilibrium constants obtained from the product ratios at high temperatures, the ratio of *cis*-III:*trans*-III at 135° is calculated to be 87.1:12.9.

The observation that *cis*-III is somewhat more stable than *trans*-III is interesting, and it deserves some further consideration. From the average equilibrium constant values at 220.0 and 198.9°, one calculates $\Delta H = -0.50$ kcal/mole and $\Delta S = +2.45$ eu for the *trans* → *cis* reaction. The very small ΔH but significantly positive ΔS for the reaction show that difference in isomer stability is primarily an entropy effect. Examination of models constructed from Bohn's data[30] indicates that the over-all rotational freedom of the methoxyl group is restricted more by H_1 and H_{3t} of *trans*-III than by H_{5c} and H_{3c} of *cis*-III.

Photolysis. Product results for the direct photolysis of Ix and In are summarized in Table III. Direct irradiation of pentane solutions of azo compound in Pyrex tubes at room temperature was accomplished with a high-pressure mercury lamp. This led to product which consisted mainly of *cis*-III and *trans*-III (combined yield >90%) with only a small amount of olefin (<5%). Extended irradiation revealed no *cis–trans* interconversion and the products were photostable under these conditions. Essentially the same product ratios were observed in the presence of air, with oxygen rigorously excluded, or in the presence of piperylene. Decomposition of *exo*-6-*d*-Ix did not lead to scrambling of the deuterium label.[25] Samples of crystalline Ix and In and glassy In[32] sealed under nitrogen in Pyrex tubes also were irradiated at low temperature (−80°).

Table IV contains the results of sensitized photolysis of Ix and In. Because of the low solubility of triphenylene the experiments were conducted in quartz tubes with 2537-Å light. At this wavelength triphenylene shows high-intensity absorption ($\epsilon \sim 10^5$).[33] Benzophenone also exhibits strong absorption ($\epsilon > 10^4$).[34] In contrast, absorptions of Ix and In at 2537 Å are weak (ϵ 60 and ϵ 35, respectively). The samples were degassed and irradiated under a nitrogen atmosphere. The major products were again *cis*-III and *trans*-III; only a small amount of what appeared to be olefinic material was detected.[35]

Several sensitized decomposition observations stand out. Triphenylene-sensitized decomposition gave somewhat different *cis*:*trans* product ratios from Ix and In. This small difference is outside of experimental

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(32) Azo compound In crystallizes only after several days at −80°. The glassy material was irradiated before crystallization had proceeded very far.

(33) H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, p 331.

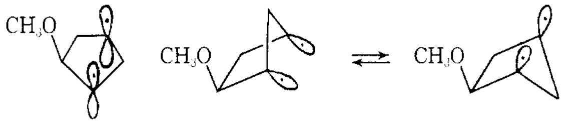
(34) Reference 1a, p 45.

(35) The direct photolysis data included in Table IV is for low conversion to product because a small change in the *cis*:*trans* product ratio occurred as the unsensitized photolysis proceeded. The ratio increased for Ix and decreased for In. This did not occur when triphenylene or benzophenone was present.

error and remained the same over more than a twofold change in sensitizer concentration. Extended irradiation showed *cis*-III and *trans*-III to be stable in the presence of triphenylene. Photolysis with triphenylene in the presence of added piperylene quencher led to *cis*:*trans* compositions identical with the ratios from direct photolysis. Benzophenone-sensitized decomposition results are strikingly different. This sensitizer produced the same *cis*:*trans* product ratio from Ix and In. Photolysis with benzophenone in the presence of piperylene did not change the product ratio but the total product formation was reduced by a factor >4 with the conditions indicated in Table IV (footnote *d*).

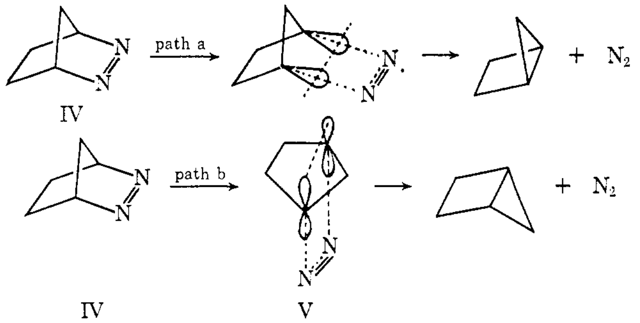
Discussion

Thermolysis. The thermolysis product results for Ix and In offer some definitive evidence regarding the question of the decomposition mechanism. Several possibilities are excluded. Failure to observe deuterium label scrambling in the products from decomposition of *exo*-6-*d*-Ix rules out neighboring group participation by the 5-methoxyl group. The fact that Ix and In give widely different *cis*-III:*trans*-III ratios leads to the conclusion that decomposition does not proceed entirely through a planar 5-methoxy-1,3-cyclopentadiyl diradical intermediate (II) common to both isomers. These results likewise preclude the sole intermediacy of an equilibrated interconverting epimeric pair of pyramidal 1,3-diradicals (IIx and IIn).



II IIx IIn

Recently, two different concerted reaction pathways have been suggested to explain the stereochemistry observed for decomposition of cyclic azo compounds[3a,36] and a related triazoline system.[5] One process involves a transition state with orbital overlap developing on the side from which nitrogen departs,[5,36] and the other involves a transition state with backside p-orbital overlap accompanying nitrogen elimination.[3a] Concerted routes involving synchronous bicyclopentane formation and nitrogen departure for the 2,3-diazabicyclo[2.2.1]-hept-2-ene system (IV) are illustrated by paths a and b. Epimers Ix and In provide stereochemical criteria for judging the importance of these paths. In path a the relationship between the C_5 methoxyl group and the C_7 carbon of the azo compound is retained in the product, whereas in path b it is inverted.

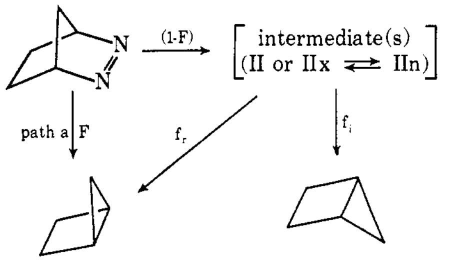


IV

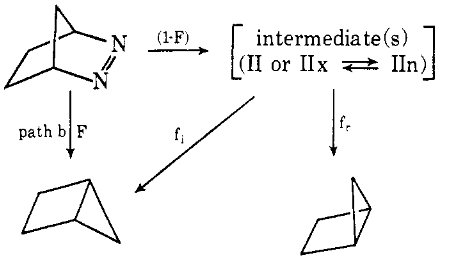
IV V

Thermolysis of Ix affords bicyclopentane product with substantial retention of configuration. In striking contrast, the product from In shows high inversion of configuration. If concerted decomposition is a major source of product, the results require that Ix and In react by different concerted pathways. Such an occurrence seems unlikely.

Scheme I



Scheme II



Reaction Schemes I and II are helpful in further evaluating the possible contributions of paths a and b to the decomposition of Ix and In. These formulations include a nonconcerted route with a nitrogen-free intermediate(s) to account for the extra product with inverted or retained configuration. In these schemes, F and $(1 - F)$ are the fractions of azo compound which react by concerted and nonconcerted paths, respectively. Fractions f_i and f_r refer to partitioning of the intermediate(s) to inverted and retained product, respectively. The values of F and $(1 - F)$ required for Scheme I or II to reproduce the *cis*-III:*trans*-III ratios observed for Ix and In may be evaluated from the data of Table II. In these calculations it is assumed that the intermediate(s) partitions to the equilibrium product composition. The resulting fractions are tabulated in Table V.

Table V. Assignment of Reaction Paths for the Thermolysis of Ix and In Based on Schemes I and II

Compd	Scheme	Fraction by reaction path			
		F	$(1 - F)$	f_i[a]	f_r[a]
Ix	I	<0	2.87	0.129	0.871
Ix	II	0.277	0.723	0.129	0.871
In	I	<0	1.07	0.871	0.129
In	II	0.504	0.496	0.871	0.129

[a] It is assumed that the intermediate(s) partitions to the 87.1:12.9 *cis*-III:*trans*-III equilibrium composition.

As shown in Table V, the $(1 - F)$ values required by Scheme I exceed 1.00 for both Ix and In. This signifies that >100% of the azo compound must react by the nonconcerted route if Scheme I is followed. Such an impossibility makes it clear that the decomposition mechanism does not include a contribution from path a.

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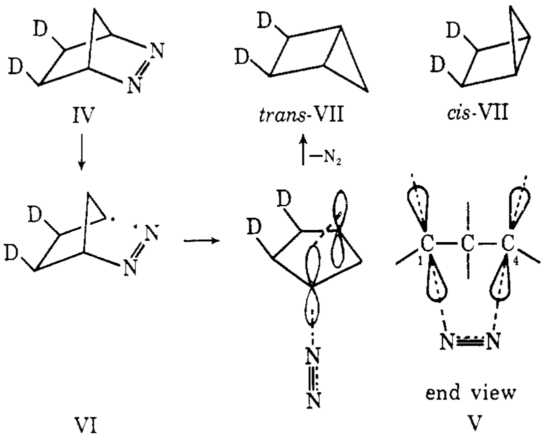
(36) T. V. Van Auken and K. L. Rinehart, *J. Amer. Chem. Soc.*, **84**, 3736 (1962).

With values of $(1 - F) < 1$ for Scheme II, it is possible to fit the product results by using path b.

The inversion of stereochemistry observed in the thermolysis of Ix and In has a very surprising aspect. Comparison of the product ratios in Table II with the equilibrium *cis*-III : *trans*-III ratio clearly shows that net inversion of product results from each isomer, *i.e.*, excess *trans*-III from Ix and excess *cis*-III from In.

Entirely analogous inversion observations have been reported by Roth and Martin.[3a,b] Thermolysis of *exo*-5,6-d_2-IV gave a 75:25 mixture of *trans*-2,3-d_2-VII and *cis*-2,3-d_2-VII. These authors have advanced two different mechanistic explanations to account for their observation. Originally inversion was ascribed to concerted elimination of nitrogen with accompanying backside p-orbital overlap in transition state V (path b above).[3a] Later they proposed that decomposition involved stepwise cleavage of the two C–N bonds with the transitory existence of a nitrogen-containing diradical VI. Inversion was attributed to the development of backside p-orbital overlap in the transition state leading from VI to nitrogen and bicyclopentane (VII).[3b]



IV

trans-VII

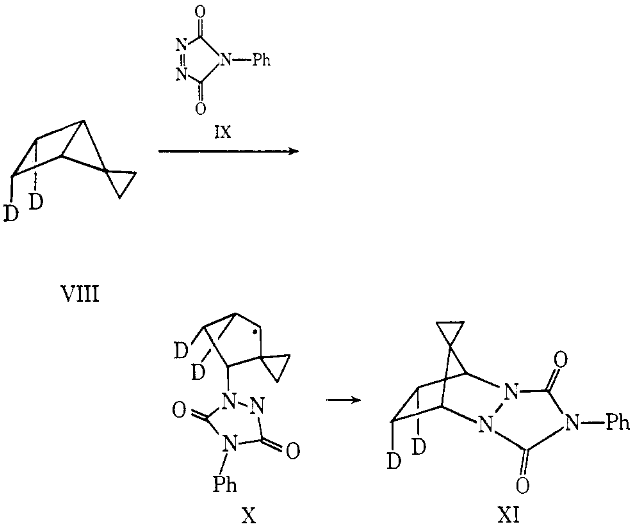
cis-VII

VI

V

Although it is possible to fit the product ratios from *exo*-5,6-d_2-IV with Scheme II, and thus account for crossover of product structure, there are several major difficulties with the proposal of transition state V. First of all, an examination of models casts considerable doubt on the idea. The geometry required for transition state V has diverging orbitals unfavorably oriented for backside overlap (see end view V). This is a consequence of a C_1 to C_4 distance of *ca.* 2.5 Å and an azo linkage going to 1.09 Å in the nitrogen molecule. Second, path b is a concerted reaction and as such falls into the Woodward–Hoffmann classification of a 2 + 2 process.[37] In this case the selection rules predict that a thermal transformation will be symmetry forbidden.[37] Furthermore, extended Hückel calculations indicate that the lowest singlet state for a planar trimethylene diradical has the two electrons in an antisymmetric combination of the p orbitals.[38] This suggests that the developing orbitals in transition state V will be antisymmetric and "antibonding." It is doubtful that such a path will favor inversion.

An explanation involving two-step cleavage of the C–N bonds satisfies the orbital symmetry criterion, but it is not supported convincingly by the argument presented[3b] or by the available evidence. This proposal is based entirely on the parallelism between the stereochemistry of *exo*-5,6-d_2-IV thermolysis and the addition of 4-phenyl-1,2,4-triazoline-3,5-dione (IX) to *cis*-2,3-dideuteriobicyclo[2.1.0]pentane-5-spirocyclopropane (VIII).[3b] In the latter regard, the mechanistic evidence indicates that addition occurs stepwise *via* the diradical intermediate X.[3b,39] The major premise seems to be that the addition reaction is the microscopic reverse of azo decomposition.[3b] Such an assumption clearly is not in keeping with the conditions of the principle of microscopic reversibility.[40] Moreover, this addition reaction is a poor model for the reverse of azo decomposition. The addition and decomposition reactions show, in fact, significantly different stereochemical results. The addition of IX to VIII occurred stereospecifically to give only inverted product XI. On the other hand, decomposition of *exo*-5,6-d_2-IV occurred with significant retention to give 25% *cis*-VII.



IX

VIII

X

XI

The elegant work of Crawford and coworkers[4] on the thermolysis of 1-pyrazolines has produced strong evidence that both C–N bonds of cyclic azo compounds are breaking in the rate-determining step and that nitrogen-free intermediates determine product stereochemistry.[41] First, there is an approximately additive effect on the decrease in activation energy in going from 1-pyrazoline to 3,3,5,5-tetramethyl-1-pyrazoline by successive methyl substitution.[4g] Such a result is to be expected if both C–N bonds are breaking in a rate-controlling transition state.[41] Second, secondary α-deuterium kinetic isotope effects provide the most convincing evidence for simultaneous cleavage of both C–N bonds. A comparison of the thermolysis rates of 3-vinyl-1-pyrazoline and the corresponding C_5-d_2 compound showed an α-deuterium effect of $k_H/k_D = 1.21$.[4d]

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(37) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965), and other references therein.

(38) R. Hoffmann, *ibid.*, **90**, 1475 (1968). R. Hoffmann informs us that the same situation holds for the planar 1,3-cyclopentadiyl diradical (private communication).

(39) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **91**, 1684 (1969); P. G. Gassman and K. T. Mansfield, *ibid.*, **90**, 1524 (1968).

(40) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 73–74.

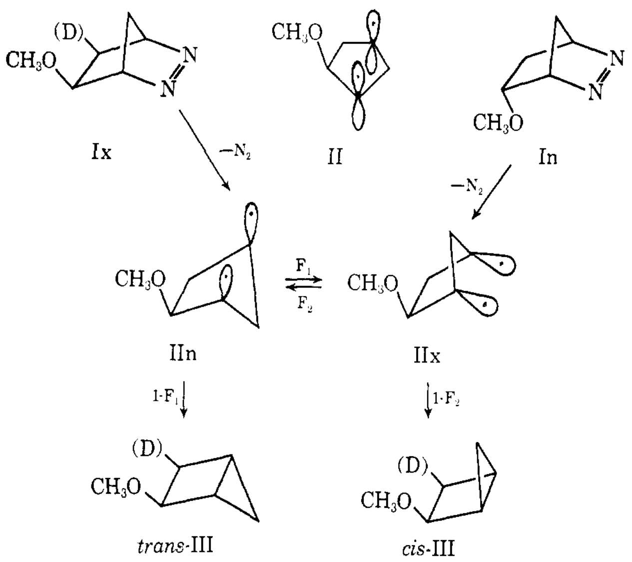
(41) For a summary of evidence for acyclic azo compounds, see C. G. Overberger, J. P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen-Nitrogen Bonds," The Ronald Press Company, New York, N. Y., 1966, pp 33–35.

Entirely analogous results were observed with either *cis*- or *trans*-3,4-dimethyl-1-pyrazoline and the corresponding C_5-d_2 compound.[4f] The comparison has been extended to include 1-pyrazoline, 1-pyrazoline-3,3-d_2, and 1-pyrazoline-3,3,5,5-d_4.[4a] It was found that the isotope effect of C_3-d_2 + C_5-d_2 is twice that of C_3-d_2. These results clearly justify the conclusion that the two C–N bonds undergo simultaneous cleavage in the rate-determining transition state.[42] Third, thermolysis of *cis*- and *trans*-3-methyl-1-pyrazoline-4-d_1 led to a 50:50 mixture of *cis*- and *trans*-methylcyclopropane-2-d_1, product ratios independent of the initial stereochemistry, and the same olefin k_H/k_D ratios from both azo epimers.[4e] These results are explained readily on the basis of an intermediate(s) which has sufficient lifetime to become completely free of nitrogen.

The Ix–In system provides some criteria for testing the Roth–Martin mechanisms.[3a,b] A consideration of the steric interaction between an *exo*-methoxyl group and a C_7 hydrogen suggests that Ix should show more inversion than IV if either mechanism is involved. If path b operates, an *endo*-methoxyl group should cause some hindrance to departure of nitrogen, and less inversion is predicted for In. Neither expectation is realized. Although the rate increases with Ix, inversion is substantially less. For In the rate decreases, but inversion is significantly greater.

A mechanism which accounts for the inversion observations and which is harmonious with all of the other available evidence as well is outlined in Scheme III. As shown, structurally inverted pyramidal diradicals IIn and IIx arise directly upon nitrogen elimination from Ix and In, respectively.[43] We propose that this inversion is a consequence of recoil from energy released by C–N bond breaking.[44] The effect can be attributed plausibly to bond rupture *via* the symmetric stretching motion of the C–N bonds.[45] The excess product of inverted structure indicates that ring closure occurs before IIn or IIx fully equilibrate. At present it is not clear whether a planar intermediate II also is involved, or if such a conformation only represents a transition state. It seems likely that II will be of higher energy than IIn or IIx because of the strain imposed by planar 1,3-carbons in a five-membered ring. The magnitude of the difference in decomposition rate suggests that little product of retained structure results by direct formation of structurally retained diradicals from Ix or In.

Scheme III



The question of the lifetime of pyramidal diradicals such as IIn and IIx is of considerable interest. It is instructive to discuss this matter in terms of the mole fractions of diradicals which invert (F) or close to product ($1 - F$) as shown in Scheme III. Equations 1 and 2 are mathematical relations which give the amounts of *trans*-III and *cis*-III formed by Ix and In, respectively. The fractions F and ($1 - F$) may be determined by adjusting the values with successive approximations until both experimentally observed product ratios are reproduced. The best values are listed in Table VI. The magnitude of these values require that IIn and IIx be

$$\%\ trans\text{-III from Ix} = 100(1 - F_1)\sum_{n=1}^{\infty}(F_1F_2)^{n-1} \quad (1)$$

$$\%\ cis\text{-III from In} = 100(1 - F_2)\sum_{n=1}^{\infty}(F_1F_2)^{n-1} \quad (2)$$

$$P = 100[(1 - F_1) + F_1(1 - F_2)] = 100[(1 - F_2) + F_2(1 - F_1)] \quad (3)$$

very short-lived. As calculated from eq 3, the per cent of product (P) arising from diradicals which close directly or invert only once and then close is 88.3%.[46] An analogous treatment of the data for *exo*-5,6-d_2-IV[3a] and XII[3b] gave very similar P values (Table VI). Such a correspondence of P values serves as a check on

Table VI. Azo Decomposition F and P Values

System	Mode of decompn	F_1	F_2	P
Ix–In	Δ	0.673	0.174	88.3
Ix–In	$h\nu^a$	0.500	0.276	86.2
exo-5,6-d_2-IV	Δ	0.333^c	0.333^c	89.0
XII^b	Δ	0.266^c	0.266^c	92.3

[a] Direct photolysis in pentane with piperylene quencher (Table III). [b] 4,5-Dideuterio-2,3-diazabicyclo[2.2.1]hept-2-ene-7-spirocyclopropane.[3b] [c] Assumed that *cis*- or *trans*-deuterium atoms do not significantly alter partitioning of the intermediates to products and thus $F_1 = F_2$.

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(42) These observations parallel the results for acyclic azo compounds.[12,41]

(43) There now is good evidence for the occurrence of nonplanar alkyl radical centers: H. M. Walborsky and C. J. Chen, *J. Amer. Chem. Soc.*, **89**, 5499 (1967); T. Ando, F. Namigata, H. Yamanaka, and W. Funaski, *ibid.*, **89**, 5719 (1967); R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965); R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963); P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Amer. Chem. Soc.*, **87**, 2590 (1965).

(44) It is interesting that Crawford and Mishra[4c] now have observed analogous net inversion of configuration in the products from thermolysis of (3*R*,5*R*)-(+)-*trans*-3,5-dimethyl-1-pyrazoline. This indicates that the recoil effect is not limited to the 2,3-diazabicyclo[2.2.1]hept-2-ene system and suggests that the phenomenon might be more general.

(45) The results of Seltzer and Mylonakis[12] suggest that the most reasonable model for the mode of decomposition of acyclic azo compounds is a symmetric stretch of both C–N bonds.

(46) This raises the question of the appropriateness of calling IIn and IIx diradicals. Crawford and Mishra[4g] have discussed this point at length for the intermediates from thermolysis of 1-pyrazolines. They conclude that such intermediates are described best as diradicals. In the case of IIn and IIx, the stereochemical results indicate that the bonding interaction between the 1,3-orbitals is not sufficient to maintain configuration. These intermediates are radical like and thus fit the definition of a "virtual diradical."[47] We have chosen to refer to the species as diradicals.

(47) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 10 (1962); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964).

Scheme III since the diradicals from the three systems should have comparable lifetimes.

Photolysis. Recent studies[4b,7a,8b,10b] indicate that the processes illustrated by eq 4–6 are involved in the photolysis of cyclic azo compounds.

$$\text{Azo} + h\nu \longrightarrow \text{Azo}^*(\text{n},\pi^* \text{ singlet excited state}) \quad (4)$$

$$\text{Azo}^* \longrightarrow \text{Azo} + h\nu_f \text{ (fluorescence)} \quad (5)$$

$$\text{Azo}^* \longrightarrow \text{N}_2 + \text{hydrocarbons} \quad (6)$$

$$\text{Azo}^* \longrightarrow \text{N}_2 + \text{Int.}^* \quad (6a)$$

$$\text{Int.}^* \longrightarrow \text{hydrocarbons} \quad (6b)$$

It has been suggested that decomposition step 6 involves loss of nitrogen to produce hydrocarbons *via* radical intermediates as shown in eq 6a and 6b.[4b,5,7a,8b] Our stereochemical observations for the photodecomposition of Ix and In are consistent with the scheme and further confirm step 4. These results also provide fundamental information about reactions 6a and 6b.

The observation that *cis*-III:*trans*-III ratios for direct photolysis of Ix and In are not altered appreciably by added triplet quenchers oxygen or piperylene suggests that decomposition occurs from an S_1, a very short-lived T_1, or a "hot" S_0 state. The substantial difference in thermolysis and photolysis product ratios is strong evidence against the last of these possibilities. A significant difference in the product ratios from direct- and triplet-sensitized photolysis excludes the second possibility. It is evident that direct irradiation produces electronically excited singlet Ix and In, and that most, if not all, product originates from this state.

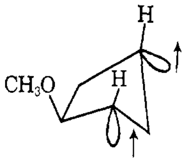
The most striking aspect of the direct photolysis results is the dependence of stereochemistry on the state of matter. In liquid solution Ix and In both exhibit crossing over of products, *i.e.*, excess *trans*-III from Ix and excess *cis*-III from In. In contrast, each epimer shows high retention of structure in the solid phase.

Any mechanistic description of the direct photoprocess must account for both stereochemical results. In this connection, the crossing over of product observation is entirely analogous to the net inversion of configuration found with thermolysis. Such similarity indicates that the two processes involve related product-forming pathways. Thus, for direct liquid phase photolysis the simplest explanation is that product also forms *via* two pyramidal diradicallike intermediates which do not survive long enough for full equilibration. Again, our best working hypothesis is that IIn and IIx arise structurally inverted from Ix and In, respectively, as a consequence of recoil from C–N bond breaking (as in thermolysis Scheme III). Since direct irradiation produces product ratios which are significantly different than those from either thermolysis or triplet sensitized photolysis it is clear that ring closure occurs at least very largely from electronically excited singlets IIn and IIx.

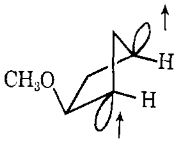
A high retention of configuration from photolysis of solid Ix and In also is in accord with the intermediacy of pyramidal species IIx and IIn. Inversion from C–N bond rupture of an electronically excited azo molecule in the crystalline state should be restricted severely because of the fixed positions of the nearest neighbor molecules. As the medium becomes less rigid and less ordered one expects a decrease in retention of configuration. These are just the stereochemical results observed on going from crystalline to glassy to liquid phase In and from crystalline to liquid phase Ix.

It is of interest to compare the behavior of the intermediates from thermolysis and direct photolysis. This may be accomplished by using an electronically excited Scheme III for photolysis and by fitting the experimentally observed solution product ratios with the aid of eq 1 and 2. Results of this treatment along with the *P* value calculated from eq 3 are listed in Table VI. Closely similar *F* and *P* values indicate S_1 and "hot" S_0 states of IIx and IIn which have comparable lifetimes. This is consistent with the occurrence of singlet species in both instances.

Benzophenone triplet-sensitized decomposition which produces the same product mixture from Ix and In could be explained mechanistically by the intermediacy of either a single triplet planar diradical or equilibrated triplet pyramidal diradicals. The ring strain considerations mentioned above suggest that pyramidal conformations will be favored. Such conformations in the present case are further favored by the repulsion factor between two electrons with parallel spins. This builtin tendency for the unpaired electrons to avoid one another is relieved most by simple conformational flexing to give IIx′ and IIn′. These conformations provide a maximum separation of electron density. If IIx and IIn species are involved, the conclusion is that the pyramidal intermediates interconvert configuration at least several times before electron spin inversion occurs. This is consistent with the triplet state having a longer lifetime than the singlet state.[5,7a,48] Some other recent evidence also suggests definable time limits for inversion of electron spin.[5,7a]



IIx′



IIn′

It is especially noteworthy that triphenylene-sensitized photodecomposition of Ix and In gives similar but not identical product distributions. In light of the quenching experiment results, this is best rationalized on the basis of concurrently occurring triplet and singlet energy transfer processes. The fact that the triphenylene-sensitized decomposition product mixtures change to the product ratios of direct photolysis when piperylene is added can be explained as being due to elimination of triplet sensitization. Further support for this comes from comparable quenching experiments of benzophenone-sensitized decomposition. In these cases, piperylene does not alter the product ratio. It is also pertinent that piperylene decreases product formation by a factor >4. Thus triphenylene-induced decomposition apparently involves sensitizer singlets as well as triplets with the Ix–In system. This indicates that triphenylene sensitization is not reliable for production of triplet intermediates in photochemical studies.

In these regards, Bartlett and Engel[8b] recently reported quantum yield evidence that triphenylene-sensitized decomposition of IV involves sensitizer singlets. They found that addition of piperylene to the triphenyl-

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[48] K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 1015 (1962).

ene-sensitized decomposition did not alter the quantum yield. In contrast, piperylene reduced the quantum yield of the benzophenone-sensitized reaction by a factor of 10. Acyclic aliphatic azo compounds also appear to react from singlet sensitization with triphenylene and other aromatic hydrocarbons.[8b,49]

Transfer of triplet excitation energy to the Ix–In system by benzophenone (E_T = 68.5 kcal) and triphenylene (E_T = 66.6 kcal) but not by pyrene (E_T = 48.7 kcal) is in complete accord with the recent estimate of ~60 kcal for the triplet of IV.[8b,9]

Experimental Section

The infrared spectra were obtained with a Beckman IR-5A spectrophotometer. Proton nmr spectra were recorded with Varian A-60 or A-56/60 spectrometers using tetramethylsilane as an internal standard. The carbon-13 magnetic resonance spectra mentioned in the Results were measured with a Varian AFS-60 spectrometer operating at 15.1 Mcps and utilizing proton-decoupling and time-averaging techniques.[27] Details of this work will appear in another paper. Ultraviolet spectra were recorded on a Beckman DK-2 spectrophotometer. The boiling points are uncorrected.

exo-**5-Methoxy-2,3-diazabicyclo[2.2.1]hept-2-ene (Ix).** To the sodium alcoholate prepared from 23 g (0.1 mole) of 2,3-dicarbomethoxy-*exo*-2,3-diazabicyclo[2.2.1]heptan-5-ol[14] and 4.4 g (0.14 mole) of sodium hydride in 420 ml of tetrahydrofuran was added 17.5 g (0.54 mole) of iodomethane. Following this the mixture was stirred under a nitrogen atmosphere at 50° for 19 hr. The excess sodium hydride was decomposed with water, most of the tetrahydrofuran was removed under reduced pressure, and the aqueous concentrate was extracted extensively with dichloromethane. After drying the combined extract over magnesium sulfate the solvent was evaporated at low pressure leaving 15 g of crude product. The absence of an OH stretching absorption at 2.90 μ[14] indicated a high conversion to 2,3-dicarbomethoxy-*exo*-5-methoxy-2,3-diazabicyclo[2.2.1]heptane.

The 15-g sample of crude 2,3-dicarbomethoxy-*exo*-5-methoxy-2,3-diazabicyclo[2.2.1]heptane in 160 ml of methanol was added to a cold solution of 35 g of potassium hydroxide in 65 ml of water. Air was removed from the system by flushing with nitrogen and lowering the pressure until the solution boiled. After several such treatments, the solution was refluxed (78°) under nitrogen for 4 hr. Most of the methanol was removed under reduced pressure and the resulting aqueous concentrate was extracted with dichloromethane. The combined extract was dried with magnesium sulfate, concentrated, and vacuum distilled giving 5.3 g of *exo*-5-methoxy-2,3-diazabicyclo[2.2.1]heptane. (In later preparations the crude hydrazine concentrate was not distilled but was oxidized directly.)

A solution of 5.3 g of the above hydrazine in 160 ml of methanol was cooled with an ice bath and 13 g of yellow mercuric oxide was added in portions with vigorous stirring. The appearance of black reduced mercury became evident within minutes. After addition, the reacting mixture was stirred at room temperature for 2 hr. The reaction mixture was filtered, treated with magnesium sulfate and decolorizing carbon, concentrated under reduced pressure, and vacuum distilled giving 4.74 g (38% over-all yield from starting alcohol) of *exo*-5-methoxy-2,3-diazabicyclo[2.2.1]hept-2-ene (Ix). An analytical sample of Ix was prepared by repeated distillation, bp 61.5° (4.5 mm). The product was found to be hygroscopic and was stored over Linde 3A 1/16-in. Molecular Sieves: uv max (cyclohexane) 341 mμ (ε 383) (–N=N–);[2a,16] ir (neat film) 6.69 μ (–N=N–);[2a,16] nmr ($CDCl_3$) complex multiplet near τ 8.7 (4 H), multiplet at 6.93 (1 H, *endo*-H_5), singlet at 6.68 (3 H, CH_3), and, broad singlets at 4.90 (1 H) and 4.72 (1 H).

Anal. Calcd for $C_6H_{10}N_2O$: C, 57.12; H, 7.99; N, 22.20. Found: C, 57.00; H, 8.04; N, 22.36.

The same procedure was used to prepare *exo*-6-*d*-Ix from 2,3-dicarbomethoxy-*exo*-2,3-diazabicyclo[2.2.1]heptan-5-ol which had been labeled specifically in the *exo*-6 position.[18] Nmr integration showed that deuterium incorporation was >90%.[18]

endo-**5-Methoxy-2,3-diazabicyclo[2.2.1]hept-2-ene (In).** A 10-g (0.043 mole) sample of 2,3-dicarbomethoxy-*endo*-2,3-diazabicyclo[2.2.1]heptan-5-ol[14] was converted to 2.44 g (45%) of *endo*-5-methoxy-2,3-diazabicyclo[2.2.1]hept-2-ene (In) by the same method used to prepare Ix. An analytical sample of In was purified by several vacuum distillations and then fractionation through an 18-in. spinning band column, bp 73.5° (2.2 mm). Since the product appeared to be hygroscopic it was stored over Linde 3A 1/16-in. Molecular Sieves: uv max (cyclohexane) 342 mμ (ε 388) (–N=N–);[2a,16] ir (neat film) 6.70 μ (–N=N–);[2a,16] nmr ($CDCl_3$) doublet with additional complex splittings at τ 9.38 (1 H), multiplet at 8.87 (2 H), eight-line pattern at 8.10 (1 H), singlet at 6.70 (3 H, CH_3), eight-line pattern at 6.00 (1 H, *exo*-H_5), multiplet at 4.92 (1 H), and multiplet at 4.60 (1 H).

Anal. Calcd for $C_6H_{10}N_2O$: C, 57.12; H, 7.99; N, 22.20. Found: C, 57.10; H, 7.88; N, 22.28.

Characterization of Products from Decomposition of Ix and In. Thermolysis and photolysis of Ix and In gave product mixture (>90% yield) which consisted of the same two components as shown by vpc analysis with a variety of columns. The nmr spectra of the mixture showed high-field proton signals above τ 9.1 and only traces of absorptions below τ 6.1. This indicates a set of isomers involving the bicyclo[2.1.0]pentane system. In this regard, the ir spectra had the expected characteristic cyclopropyl absorptions in the 3.25–3.3- and 9–10-μ regions.[2a,50] A degassed sample of Ix was decomposed thermally and was analyzed directly without further purification.

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.24; H, 10.21.

Isolation of the two components was achieved by preparative vpc separation (20 ft × 0.25 in. column packed with 15% tetraethylene glycol on Chromosorb P) of a 52:48 product mixture obtained from the photolysis of neat Ix. The early and late eluting isomers were identified as *trans*-2-methoxybicyclo[2.1.0]pentane (*trans*-III) and *cis*-2-methoxybicyclo[2.1.0]pentane (*cis*-III), respectively, on the basis of the evidence cited in the Results. The proton nmr spectral data ($CDCl_3$) for *trans*-III were: doublet of triplets at τ 9.45 (1 H, w_h = 7 cps, H_{5c}), multiplet at 9.15 (1 H, w_h ~ 17–19 cps, H_{5t}), multiplet at 8.25 (4 H), singlet at 6.68 (3 H, CH_3), multiplet near 6.6 (1 H, H_{2c}), and for *trans* C_3 deuterium labeled *trans*-III multiplet at 8.25 (3 H). The proton nmr spectral data ($CDCl_3$) for *cis*-III were: multiplet at τ 9.41 (1 H, w_h ~ 17–19 cps, H_{5t}), doublets of triplets at 9.16 (1 H, w_h ~ 7 cps, H_{5c}), four-line pattern with additional splittings at 8.77 (1 H), multiplet at 8.55 (1 H), multiplet at 8.18 (1 H), 16-line pattern at 7.76 (1 H), singlet at 6.85 (3 H, CH_3), quintet with additional splittings at 6.10 (1 H, H_{2t}), and for *cis* C_3 deuterium labeled *cis*-III multiplet missing at 8.77.

Thermolysis Kinetics. Thermal decomposition rate measurements were made by using vpc analysis to follow the development of product against 1,2-dimethoxyethane as an internal standard. Samples of 10 μl of a 30 vol % solution of 1,2-dimethoxyethane in azo compound in 1-ml thick-walled Pyrex tubes were degassed and sealed under nitrogen at *ca.* 0.6 mm. For a given rate determination, a set of tubes were simultaneously immersed in a constant-temperature silicone oil bath controlled at ±0.05°. At regular intervals over the first 80% decomposition tubes were removed and quenched with a Dry Ice–acetone bath. A total of five or more points were obtained over this decomposition range. The samples were analyzed with a vpc column which showed *cis*-III and *trans*-III as a single combined peak (5 ft × 0.25 in. column packed with Carbowax 20M on Chromosorb P).

Analysis of Product Mixtures. Analyses of the product mixtures from thermolysis and photolysis of Ix and In and thermal equilibration of *cis*-III and *trans*-III were performed with either a 20 ft × 0.125 in. or 20 ft × 0.25 in. vpc column packed with 15% tetraethylene glycol on Chromosorb P.

Thermolysis Products. The product compositions for gas-phase decomposition of Ix and In were obtained from 5–6-μl samples of azo compound which had been degassed and sealed under nitrogen at *ca.* 0.6 mm in 25- and 250-ml Pyrex tubes. The tubes were heated at 135° for 30 hr (*ca.* 5 half-lives) for Ix and for 100 hr (*ca.* 2.5 half-lives) for In. After decomposition, the product was collected for vpc analysis by cooling an attached side-arm capillary tube in a Dry Ice–acetone bath. The values reported in Table II are averages of the results from the experiments with 25- and 250-ml tubes.

Thermal Equilibration of ***cis*****-III and** ***trans*****-III.** These determinations were made by the same method used for the measurement of

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thermolysis products. Individual samples of Ix, In, and a 47.9:52.1 mixture of *cis*-III and *trans*-III were heated at 198.9° for 16 hr. Samples of Ix and In also were heated at 220° for 5.5 hr. A sample of the 47.9:52.1 mixture of *cis*-III and *trans*-III was heated at 135° for 100 hr as a check on product isomerization under thermolysis product conditions.

Direct Photolysis Products. The following illustrates the general procedure used to determine the product composition from direct irradiation of Ix and In in solution. A 5-ml sample of a 0.01 M solution of azo compound in pentane in a 10-ml Pyrex tube was degassed by three freeze-pump-thaw cycles and sealed under *ca.* 0.6 mm nitrogen. The sample tube was taped to a water-cooled quartz immersion well and irradiated for 24 hr with a 200-W Hanovia Type S lamp. Following irradiation the sample was analyzed directly by vpc. A pentane solution 0.3 M in piperylene was used for the quenching experiments.

Solid-phase direct photolysis was accomplished with samples of azo compound which had been degassed and sealed under nitrogen in Pyrex tubes. A sample tube was strapped to a transparent Pyrex vacuum dewar flask which then was immersed in a Dry Ice-methanol bath at -80°. After crystallization appeared to be complete[32] the sample was irradiated for 15 hr with the 200-W lamp. The lamp was placed directly in the dewar flask and was cooled with a stream of air.

Sensitized Photolysis Products. The following is typical of the procedure used for the sensitized photodecomposition studies of Ix and In. Samples (5 ml) of cyclohexane solutions 0.01 M in azo compound and 0.05 M in benzophenone were placed in 20-ml quartz test tubes having 14/20 standard taper joints on the top. The tubes fitted with a stopcock were degassed by three or more freeze-pump-thaw cycles and closed under *ca.* 0.6 mm nitrogen. Irradiation was performed on a "merry-go-round" assembly in a Rayonet-Griffin-Srinivasan photochemical reactor using a 2537-Å light source. Experiments with and without piperylene were carried out simultaneously under identical conditions. Following irradiation, analyses were performed by vpc on product solutions which had been flash distilled (kettle temperature *ca.* 60°) under low vacuum into a Dry Ice-acetone-cooled trap.

For sensitized decompositions conversion to product was complete in <20 min. This was estimated by vpc by measuring the development of product against 1,2-dimethoxyethane as an internal standard. The ratio of products formed in the presence of sensitizer did not change during irradiation times from 5 to 75 min.[35]

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Thermal Rearrangements of Some 1,3-Methanoindans (Benzobicyclo[2.1.1]hexenes)[1]

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Abstract: 1,3-Methanoindan (**1**) thermally isomerizes to 1,1a,6,6a-tetrahydrocycloprop[*a*]indene (**2**) in a quantitative yield. In the case of the *anti*-2-chloro derivative (**3**), the reaction proceeds with a quantitative formation of naphthalene. When the reaction was carried out with methyl *anti*-2-chloro-1,3-methanoindan-*exo*-8-carboxylate (**5**) (or its *endo* isomer (**8**)), the products were a 20% yield of methyl α-naphthalenecarboxylate (**6**) and a 55% yield of methyl β-naphthalenecarboxylate (**7**) (or 5% **6** and 80% **7**). The rates and activation parameters of the reactions were determined. Relative to the parent **1**, the monosubstituted **3** and methyl 1,3-methanoindan-*endo*-2-carboxylate (**19**) react at rates enhanced by factors of 40–50. However, the rate of the disubstituted **5** was approximately only twice as much as those of **3** and **19** and that of **8** was not significantly different from those of **3** and **19**. The results are discussed in radical mechanisms as well as a [1,3]-sigmatropic rearrangement.

Derivatives of 1,3-methanoindan, the smallest bridged benzocyclene known, were first synthesized by us[2] and Pomerantz,[3] independently. The solvolytic behavior of the derivatives and evidence for large participation of the benzene ring were recently reported.[4] As a continuation of our research on this ring system, this paper deals with the behavior in thermolysis.

Results

The syntheses of all but one reactants employed were reported by us.[2,4] The exception was prepared according to substantially the same methods as above (Experimental Section). Heating a carbon tetrachloride solution of 1,3-methanoindan (**1**) at 200° for 15 hr (9 half-lives) in a tube sealed under nitrogen atmosphere gave a single product as analyzed by vpc. The product was isolated and its structure established to be 1,1a,6,6a-tetrahydrocycloprop[*a*]indene (**2**) by comparison with an authentic sample.[5] The yield estimated by vpc was roughly quantitative. When the reaction was carried out with *anti*-2-chloro-1,3-methanoindan (**3**), a quantitative formation of naphthalene (**4**) was observed. It is therefore reasonable to consider that a chloro derivative(s) of **2** or an intermediate(s) leading to it (them) converts into **4** with elimination of hydrogen chloride under the reaction conditions.

Of special interest is that the reaction with methyl *anti*-2-chloro-1,3-methanoindan-*exo*-8-carboxylate (**5**) (160°, 5 hr which corresponds to 6 half-lives) produced methyl α-naphthalenecarboxylate (**6**) in 20% yield and its β isomer (**7**) in 55% yield and the reaction with the

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