thermodynamics associated with the ring-flattening feature, and possibly some of the variations in ΔH and ΔS in Table II are associated with changes in the extent of pucker in the central ring.

Conclusion

This study has demonstrated the manner in which both liquid and solid high-resolution NMR methods can be used as complementary techniques in conformational and structural analysis. Freezing of a pure conformational structure in the solid state provides specific structural shift parameters for characterizing molecules with highly mobile conformations in the liquid state. The thermodynamic quantities obtained from the temperature-dependent liquid chemical shifts were thus corroborated by this dual approach.

It was found that the chemical shifts for the parent and mono- and dimethyl-substituted 9,10-dihydroanthracenes could all be rationalized with standard methyl substituent parameters. Chemical shift deviations for the tri- and tetramethyl derivatives could be explained in terms of ring flattening of the central ring. Failure to find clearly distinguishable axial and equatorial methyls for the tetramethyl compound in the solid state indicated the general structural similarity of all methyls in this compound and suggested a planar or near planar structure for this highly methylated species. The close similarity of liquid and solid parametric shifts argues strongly for the similarity of the structural features in both the solid and liquid states. Should the crystal packing forces have resulted in major conformational changes between the solid and liquid, these would have led to greater discrepancies between the liquid and solid parametric shifts. Even though the solid and liquid conformations for a given compound are very similar when proper consideration is given to the dynamic averaging taking place in the liquid, the data clearly indicate that the degree of puckering for the central ring does vary considerably between members of this series. This conformational flexibility undoubtedly is one of the unique features of the 9,10-dihydroanthracenes and the other related hydroaromatic molecules.

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Decomposition and Isomerization of Bridgehead Cis 1,2-Diazenes (Azoalkanes)[1]

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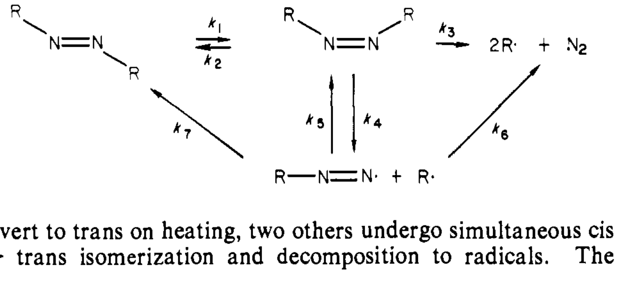
Abstract: Four acyclic cis 1,2-diazenes, azo-1-adamantane (*cis*-ada), azo-1-bicyclo[2.2.2]octane (*cis*-[2.2.2]), azo-1-bicyclo[2.2.1]heptane (*cis*-[2.2.1]), and azo-1-bicyclo[2.1.1]hexane (*cis*-[2.1.1]) have been generated by UV irradiation of the corresponding trans isomers. These compounds differ greatly in stability, *cis*-[2.1.1] easily surviving at 100 °C and *cis*-ada not being isolable. Whereas *cis*-[2.1.1] and *cis*-[2.2.1] only isomerize back to trans on heating, the other two compounds undergo competing loss of nitrogen. The observation that the energy of the transition state for isomerization remains at 42 ± 1 kcal mol^{-1} regardless of the cis ground state energy is used to argue that thermal isomerization proceeds via semilinearization rather than rotation. A remarkable correlation of cis ground state energy with cis n,π* excitation energy has emerged from this study.

It has been known for over 40 years that irradiation of *trans*-diaryldiazenes (azobenzenes, *trans*-Ar–N=N–Ar) produces the cis isomers, which revert to trans on mild heating.[2] Since thermal cis → trans isomerization is exothermic by about 12 kcal mol^{-1}, the cycle trans $\xrightarrow{h\nu}$ cis $\xrightarrow{\Delta}$ trans has been considered for solar energy storage.[3,4] Diaryldiazenes have also been incorporated as photosensitive groups to control the properties of crown ethers, membranes, and related species.[5]

Aliphatic[6-10] and alkylaryl[11,12] cis diazenes are of more recent vintage and their chemistry is more varied than that of the diaryldiazenes. Thus, *cis*-dialkyldiazenes can isomerize directly to trans or they can decompose by stepwise or simultaneous C–N bond cleavage. Most of these compounds are thermally labile but *cis*-dimethyldiazene and *cis*-diisopropyldiazene have been isolated.[7,8]

Scheme I. Reaction Pathways of Cis Diazenes



The goals of the present research were to prepare stable *cis*-dialkyldiazenes and to study the effect of structure on their thermal behavior. As will be seen below, some of these new diazenes are not only more stable than *cis*-azobenzene but they liberate more heat during the isomerization process. Whereas two of them only revert to trans on heating, two others undergo simultaneous cis → trans isomerization and decomposition to radicals. The

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(1) For a preliminary report of this work, see Engel, P. S.; Melaugh, R. A.; Page, M. A.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 1971.

(2) Hartley, G. S. *Nature (London)* **1937**, *140*, 281; Talaty, E. R.; Fargo, J. C. *J. Chem. Soc., Chem. Commun.* **1967**, 65; Golson, T. H.; Ph.D. Dissertation, University of New orleans, 1971.

(3) Fisher, D. P.; Piermattie, V.; Dabrowiak, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2811.

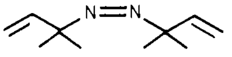
(4) Adamson, A. W.; Vogler, A.; Kunkely, H.; Wachter, R. *J. Am. Chem. Soc.* **1978**, *100*, 1298.

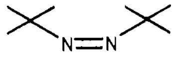
(5) Shinkai, S.; Nakaji, T.; Ogawa, T.; Shigematsu, K.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 111.

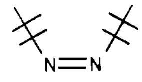
0002-7863/81/1503-4824$01.25/0

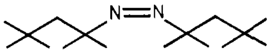
thermodynamics of both reactions are now rather well understood.

In choosing the *cis*-dialkyldiazenes to be studied, we considered two factors which could affect their rate of disappearance: the stability of the radicals (R·) resulting from deazatization and the steric bulk of the alkyl (R) groups. The rate constants k_3 or k_4 in Scheme I should increase when R· is a more stable radical, as seen in trans diazenes[13,14] and in **1** ($t_{1/2}$ = 10 min at −120 °C) vs. *cis*-azo-*tert*-butane (ATB) ($t_{1/2}$ = 10 min at −11 °C).[10]


1


cis-ATB

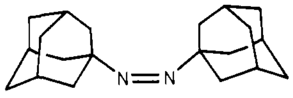

2


3

Greater steric bulk of the R group is also known to accelerate k_3 or k_4; for example, **2** undergoes thermolysis at −28 °C, 1600 times faster than *cis*-ATB.[15] Similarly, $t_{1/2}$ for decomposition of **3** is 10 min at −70 °C, whereas ATB exhibits the same half-life at −11 °C.[10] Since *trans*-**2** decomposes only 3–6 times faster than *trans*-ATB,[14,15] this steric effect is far more pronounced in the cis isomers than in the trans. Direct cis → trans isomerization (k_2) is also expected to slow down as R becomes smaller, due to lowering of steric repulsion and thus of the cis ground state energy. These considerations suggest that the most stable cis diazene will result if R· is a small and highly unfavorable free radical.

An additional factor in selecting appropriate compounds was that diazenes possessing α protons tend to tautomerize. *cis*-Dimethyldiazene, a likely candidate from the standpoint of alkyl size and methyl radical instability,[16] tautomerizes at room temperature to formaldehyde methylhydrazone, which then undergoes self-condensation.[17] The obvious solution of using a simple tertiary diazene (ATB) is unsatisfactory because of its aforementioned lability.[9,10]

With these considerations in mind, we selected for study the cis bridgehead diazenes azo-1-adamantane (*cis*-ada), azo-1-bicyclo[2.2.2]octane (*cis*-[2.2.2]), azo-1-bicyclo[2.2.1)]heptane (*cis*-[2.2.1)], and azo-1-bicyclo[2.1.1]hexane (*cis*-[2.1.1], which clearly cannot tautomerize. Since the number of bridging carbons diminishes along this series, the effective steric bulk[18] of R and hence the value of k_3 (or k_4) and k_2 should decline steadily. Finally, rate data obtained by Rüchardt for the trans isomers indicate decreasing ease of radical formation in the same order. k_{rel} (trans, 300 °C): *cis*-ada (1.0), *cis*-[2.2.2] (0.13), *cis*-[2.2.1] (0.008).[13] It has been suggested recently that these thermolysis rates are determined not only by incipient radical stability but also by the requirement for planarity in the transition state for deazatization.[13,19,20]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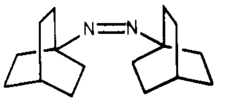
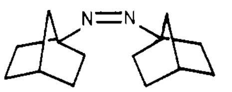

cis-[2.2.2]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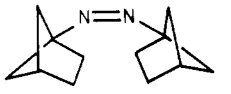
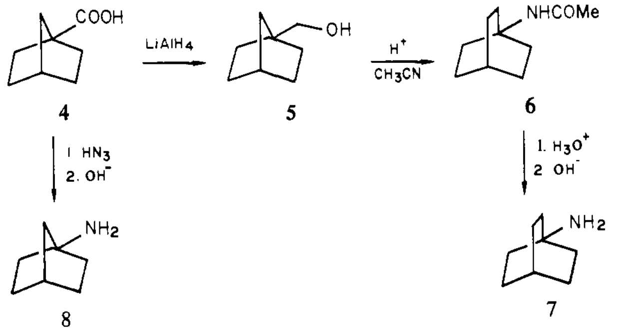
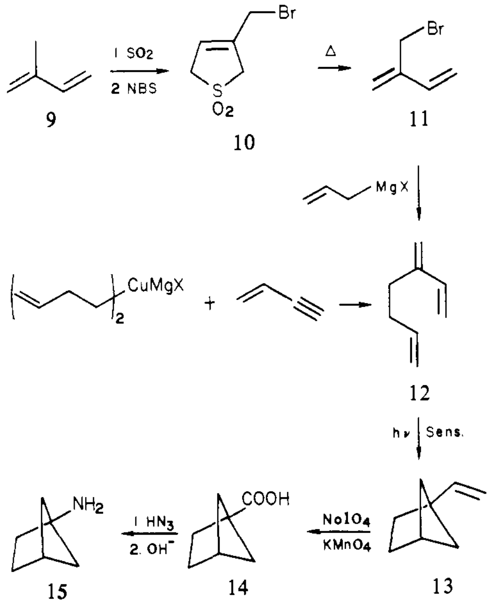

cis-[2.1.1]

Synthesis of 1,2-Diazenes

With the exception of *trans*-[2.1.1], the trans diazenes used in this study are known compounds[13] and were prepared from the sulfamides by the Stowell modification[21] of the Ohme–Preuschhof procedure.[22] The sulfamides were in turn prepared from the amines. Norbornane-1-carboxylic acid (**4**)[13,23,24] was the precursor for two of the required amines, **7** and **8**. Whereas conversion of **4** to 1-aminonorbornane (**8**) is a known reaction,[13] the synthesis of **7** shown below represents an improvement over the previous methods.[25,26] The ring-expanding Ritter reaction on which it is based has good precedent in other reactions of **5**.[27,28] 1-Aminobicyclo[2.1.1]hexane (**15**) was prepared by photocyclization of triene **12**[29] with subsequent oxidation to acid **14** followed by a Schmidt reaction. The requisite triene **12** was made by two





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(6) For a review of alkyl diazenes, see Engel, P. S. *Chem. Rev.* **1980**, 99.

(7) Fogel, L. D.; Rennert, A. M.; Steel, C. *J. Chem. Soc., Chem. Commun.* **1975**, 536.

(8) Abram, I. I.; Milne, G. S.; Solomon, B. S.; Steel, C. *J. Am. Chem. Soc.* **1969**, *91*, 1220.

(9) Mill, T.; Stringham, R. S. *Tetrahedron Lett.* **1969**, 1883.

(10) Engel, P. S.; Bishop, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 6754.

(11) Porter, N. A.; Marnett, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 4361.

(12) Porter, N. A.; Dubay, G. R.; Green, J. G. *J. Am. Chem. Soc.* **1978**, *100*, 920.

(13) Golzke, V.; Groeger, F.; Oberlinner, A.; Rüchardt, C. *Nouv. J. Chim.* **1978**, *2*, 169.

(14) Bandlish, B. K.; Garner, A. W.; Hodges, M. L.; Timberlake, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 5856.

(15) Schulz, A.; Rüchardt, C. *Tetrahedron Lett.* **1977**, 849.

(16) Rice, O. K.; Sickman, D. V. *J. Chem. Phys.* **1936**, *4*, 242.

(17) Ackerman, M. N.; Craig, N. C.; Isberg, R. R.; Lauter, D. M.; MacPhail, R. A.; Young, W. G. *J. Am. Chem. Soc.* **1977**, *99*, 1661.

(18) Beckhaus, H. D. **1978**, *17*, 592; Giese, B.; Beckhaus, H. D. *Ibid.* **1978**, *17*, 594.

(19) Firestone, R. A. *J. Org. Chem.* **1980**, *45*, 3604.

(20) Hinz, J.; Rüchardt, C. *Justus Liebigs Ann. Chem.* **1972**, *765*, 94.

(21) Stowell, J. C. *J. Org. Chem.* **1967**, *32*, 2360.

(22) Ohme, R.; Preuschhof, H. *Justus Liebigs Ann. Chem.* **1968**, *713*, 74; Ohme, R.; Preuschhof, H.; Heyne, H. U. *Org. Synth.* **1972**, *52*, 11.

(23) Boehme, W. R. *J. Am. Chem. Soc.* **1959**, *81*, 2764.

(24) Bixler, R. L.; Niemann, C. *J. Org. Chem.* **1958**, *23*, 742.

(25) Fischer, H. P.; Grob, C. A. *Helv. Chim. Acta* **1964**, *47*, 564.

(26) Kauer, J. C.; U.S. Patent 3 546 290, 1968; *Chem. Abstr.* **1971**, *74*, 141109g.

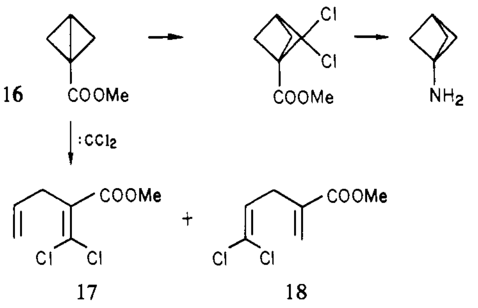
(27) Humphrey, C. B.; Hodgson, B.; Pincock, R. E. *Can. J. Chem.* **1968**, *46*, 3099.

(28) Applequist, D. E.; Kaplan, L. *J. Am. Chem. Soc.* **1965**, *87*, 2194.

(29) Wiberg, K. B.; Lowry, B. R. *J. Am. Chem. Soc.* **1963**, *85*, 3188.

routes, starting with isoprene or vinylacetylene. Although the first method (**9** → **12**) involved more steps, it proved to be superior for large-scale preparations. Considerable effort was expended to determine the optimum conditions for photocyclization of the triene (cf. the Experimental Section).

It should be mentioned parenthetically that attempts to prepare azo-1-bicyclo[1.1.1]pentane were abandoned when carbene addition to ester **16** gave mainly olefins **17** and **18**. Although early reports[30] on this addition were discouraging, Applequist's success with related compounds[31] and the advent of phase transfer techniques for generating carbenes[32] stimulated us to repeat it.



A point of synthetic interest is that oxidation of the sulfamide which should have led to *trans*-[2.1.1] gave both cis (22%) and trans (62%) isomers. The only previously reported sulfamide which produced any cis diazene was the diisopropyl compound.[33] These results suggest that other sulfamides might go partially to cis diazenes which extrude nitrogen or tautomerize under the reaction conditions. Alternately, the general failure to obtain cis diazenes could reflect the instability of the corresponding *cis*-thiadiaziridine 1,1-dioxides,[34] whose trans isomers have been postulated as intermediates in this oxidation of sulfamides.[35] Despite several attempts, we have been unable to isolate and characterize any *cis*-thiadiaziridine 1,1-dioxide.

The cis diazenes were generated by irradiation of the trans isomers in the region of 366 nm. A Corning 7-54 filter was used to remove visible light, thereby diminishing the reverse photoisomerization of cis to trans and allowing a higher stationary state cis concentration to be achieved. Since the absorption spectrum of the cis diazenes extends into the visible region, it is hardly surprising that *cis*-[2.1.1] reverts readily to trans during storage in ambient light but is stable for weeks in the dark. Whereas *cis*-ada was too thermally unstable to isolate, *cis*-[2.2.1] and *cis*-[2.1.1] were obtained as stable crystalline solids, the latter of which could even be sublimed. *cis*-[2.2.1] melted sharply at 92.5–93.5 °C and further heating of the yellow melt at 110–115 °C caused resolidification to a white solid which remelted sharply at 166–167 °C, the exact melting point of pure trans. *cis*-[2.1.1] melted at 89–90 °C and darkened upon heating to 150 °C.

Results

Kinetics. As shown in Figure 1, irradiation of *trans*-ada in the cold led to formation of a 455-nm band attributed to *cis*-ada. The intensity of this band was 6 times larger that the decrease in trans absorbance (368 nm) because the n–π^* transition in cis diazenes is always more strongly allowed than in trans.[36] Rate constants for disappearance of c-ada and the other cis diazenes (Table I) were obtained by simply warming the solution to a constant temperature and monitoring the cis absorption band. Interpretation of the rate data in raw form is not particularly useful because the rates for *cis*-ada and *cis*-[2.2.2] are the sum of two independent processes: isomerization to trans and decomposition. For *cis*-[2.2.1] and *cis*-[2.1.1] no nitrogen is evolved, the only thermal process being isomerization.

Table I. Rate Data for Disappearance of Bridgehead Cis Diazenes[a]

compd	10^4k, s^{-1}	temp, °C	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, eu
cis-ada	1.97	18.4	25.9 ± 0.5	13.3 ± 1.6
	2.82	21.0		
	4.07	23.3		
	6.03	26.0		
	9.16	28.4		
	13.3	31.4		
	3.69[b]	26.0		
cis-[2.2.2]	0.229	17.5	25.9 ± 0.3	9.3 ± 0.9
	0.304	19.2		
	0.344	20.1		
	1.333	28.4		
	1.374	29.9		
	4.624	38.2		
	5.715	39.4		
	18.22	48.1		
	19.64	48.7		
cis-[2.2.1]	0.857	79.5	30.9 ± 0.5	12.0 ± 1.3
	0.818	81.2		
	0.885	81.5		
	1.648	84.6		
	3.875	91.2		
	2.933	91.5		
	3.167	91.8		
	4.388	92.1		
	8.015	97.5		
	9.983	102.1		
	9.15	102.3		
	9.167	101.8		
cis-[2.1.1]	1.286	125.0	30.3 ± 0.5	0.8 ± 1.3
	2.300	131.1		
	3.787	136.6		
	5.462	139.8		
	10.20	148.2		
	11.02	148.5		
	12.65	150.4		
	26.92	158.0		
	27.36	158.1		

[a] In xylene by UV spectroscopy. [b] In 2-propanol.

Data listed in Table II indicate the fate of *cis*-ada as a function of solvent and temperature. These values were obtained by UV comparison of the amount of trans which disappeared on irradiation in the cold to the amount which reappeared after the solution had been warmed long enough for all cis to react (cf. Figure 1). By actually measuring the nitrogen evolved from such solutions, we demonstrated that the trans which failed to reappear was accounted for as nitrogen produced. These results are shown in Table III.

If toluene and xylene are assumed to be equally polar, one can combine the data in Tables I and II to deduce individual rate constants for isomerization and decomposition of *cis*-ada. The percent cis → N_2 values in Table II were merely interpolated to the temperatures used for kinetic runs and multiplied by the observed rate constants for cis disappearance. An Eyring treatment of the resulting rate constants (Table IV) provided the activation parameters for the two competing reactions.

It was of interest to compare isomerization rates of the bridgehead diazenes; therefore, the kinetic data for *cis*-[2.2.1] and *cis*-[2.1.1] were extrapolated to 25 °C where the values for *cis*-ada had been determined. Combined with a single measurement for *cis*-[2.2.2], these results are shown in Table V. Relative rate constants for the deazatization of *cis*-ada and *cis*-[2.2.2] were calculated easily from the foregoing data and are compiled in Table VI.

Differential Scanning Calorimetry Measurements. The melting behavior of *cis*-[2.2.1] suggested that its cis–trans enthalpy difference, ΔH_{isom}, might be determined directly by differential scanning calorimetry (DSC). In principle, each determination

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[30] Wiberg, K. B.; Lampman, G. M.; Ciula, R. P.; Conner, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749.
[31] Applequist, D. E.; Wheeler, J. W. *Tetrahedron Lett.* **1977**, 3411.
[32] Starks, C. W. "Phase Transfer Catalysis"; Academic Press: New York, 1978.
[33] Engel, P. S. *Tetrahedron Lett.* **1974**, 2301.
[34] Timberlake, J. W.; Alender, J.; Garner, A. W.; Hodges, M. L.; Özmeral, C.; Szilagyi, S.; Jacobus, J. O. *J. Org. Chem.* **1981**, *46*, 2082.
[35] Ohme, R.; Schmitz, E. *Angew Chem., Int. Ed. Engl.* **1965**, *4*, 433.
[36] Rau, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 224.

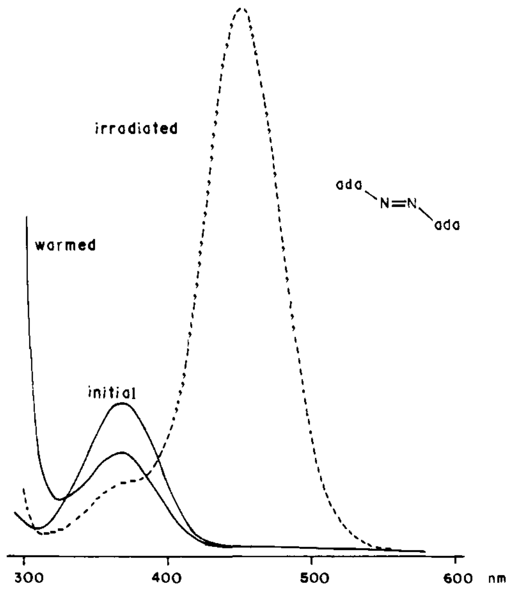

Figure 1. Absorption spectrum of azo-1-adamantane. Initial = trans isomer at −10 °C before UV irradiation. Irradiated = mixture of cis and trans isomers produced by irradiation. Warmed = after warming and disappearance of the cis isomer. Note that only part of the initial trans isomer is regenerated.

Table II. Fate of *cis*-Ada as a Function of Solvent and Temperature[a]

solvent	E_T[b]	temp, °C	% cis → N_2
hexane	30.9	0.0	51.1
		12.0	56.3
		23.5	63.0
		38.0	68.5
		38.0	69.5
toluene	33.9	0.0	31.9
		12.0	41.7
		24.5	49.9
		34.5	57.9
acetone	42.2	11.5	30.1
		18.0	33.4
		24.5	39.0
		33.0	44.5
		35.0	48.3
2-propanol	48.6	0.0	4.6
		12.0	7.3
		26.0	13.0
		34.0	16.9
		36.0	18.7

[a] Determined by UV spectroscopy. [b] Solvent polarity; cf. Reichardt, C. *Angew. Chem., Int. Ed. Engl.* 1979, *18*, 98.

Table III. Fate of *cis*-Ada by Nitrogen Evolution vs. UV Spectroscopy[a]

temp, °C	% cis → N_2[b]	% cis → N_2[c]
14.0	52.5	49.7
25.5	57	58.3
36.75	67.7	69.9

[a] In hexane. [b] By nitrogen evolution. [c] By UV spectroscopy.

consists of two DSC scans over the same temperature range, the first process being

$$\text{cis(s,T}_1) \rightarrow \text{trans(s,T}_2) \qquad \Delta H_\text{I}$$

which, after cooling of the trans formed, is followed by

$$\text{trans(s,T}_1) \rightarrow \text{trans(s,T}_2) \qquad \Delta H_\text{II}$$

where s = solid. Taking the difference yields

$$\text{cis(s,T}_1) \rightarrow \text{trans(s,T}_1) \qquad \Delta H_\text{isom}(\text{s,T}_1) = \Delta H_\text{I} - \Delta H_\text{II}$$

In practice, the second scan gave the same base line as one would draw for the first scan; hence, peak areas were measured using only one scan and base lines generated by computer graphics. After it was demonstrated that the area of the exotherm from freezing indium exactly equalled that of the endotherm produced by melting, several known compounds were run to ensure the accuracy of our technique (cf. Table IX). DSC traces for *cis*-[2.2.1] and three other cis diazenes are shown in Figure 2 and the results are summarized in Table VII.[37] We also attempted

Table IV. Dissection of the Rate Constant for Disappearance of *cis*-Ada into Those for Individual Competing Reactions

temp, °C	$10^4 k_\text{dec}$, s^{-1}[a]	$10^4 k_\text{isom}$, s^{-1}[b]	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu
18.4	0.898	1.07	28.5 ± 0.5[a]	20.5 ± 1.5[a]
21.0	1.34	1.48		
23.3	2.00	2.07	23.2 ± 0.5[b]	3.0 ± 1.6[b]
25.98	3.10	2.93		
28.41	4.85	4.31		
31.38	7.34	5.96		

[a] For decomposition to N_2. [b] For isomerization to trans.

Table V. Absorption Maxima[a] and Relative Rates of Diazene Cis → Trans Isomerization[b] at 25 °C

compd	trans λ_max	cis λ_max	% cis → trans	rel k_isom
cis-ada	368	455	50%	(1.0)
cis-[2.2.2]	369	444	98%	2.4×10^{-1}
cis-[2.2.1]	365	423	100%	2.1×10^{-4}
cis-[2.1.1]	371	404	100%	2.0×10^{-6}

[a] In hexane, nm. [b] In toluene.

Table VI. Comparison of Deazatization Rates of Cis and Trans Diazenes

compd	k_rel(cis), 25 °C[a]	k_rel(trans), 300 °C
ATB	(1.0)[b]	1
ada	2.0×10^{-4}[c]	4.0×10^{-4}
[2.2.2]	5.0×10^{-6}[c]	5.0×10^{-5}

[a] In hexane. [b] Absolute calculated rate is 2.02 s^{-1} from data in ref 48. [c] See ref 49 for method of calculation.

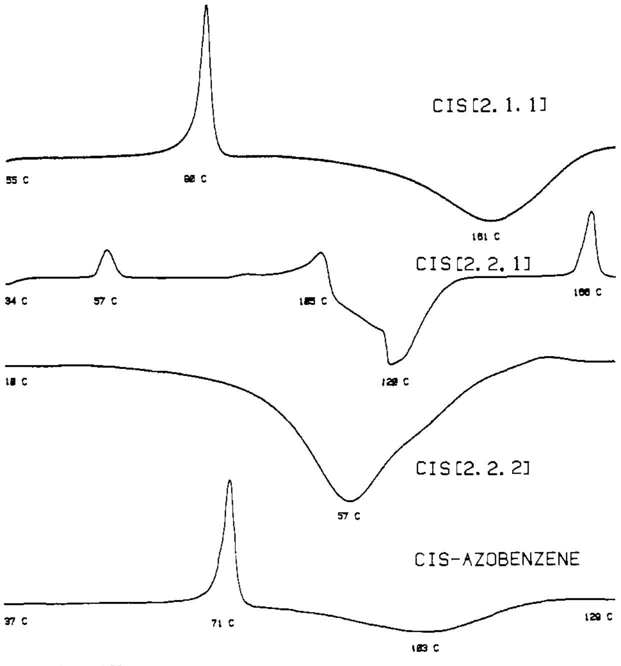

Figure 2. Differential scanning calorimeter traces obtained on cis 1,2-diazenes. A downward pen deflection indicates an exothermic process.

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[37] A value of −12.6 kcal mol^{-1} for ΔH_isom of *cis*-[2.2.1] was reported earlier,[1,6,38] but it appears to be too low, possibly because the sample isomerized during shipment. This work was of value nevertheless because the high purity found for reformed trans (99.80%) demonstrated that thermal isomerization of cis was not accompanied by decomposition.

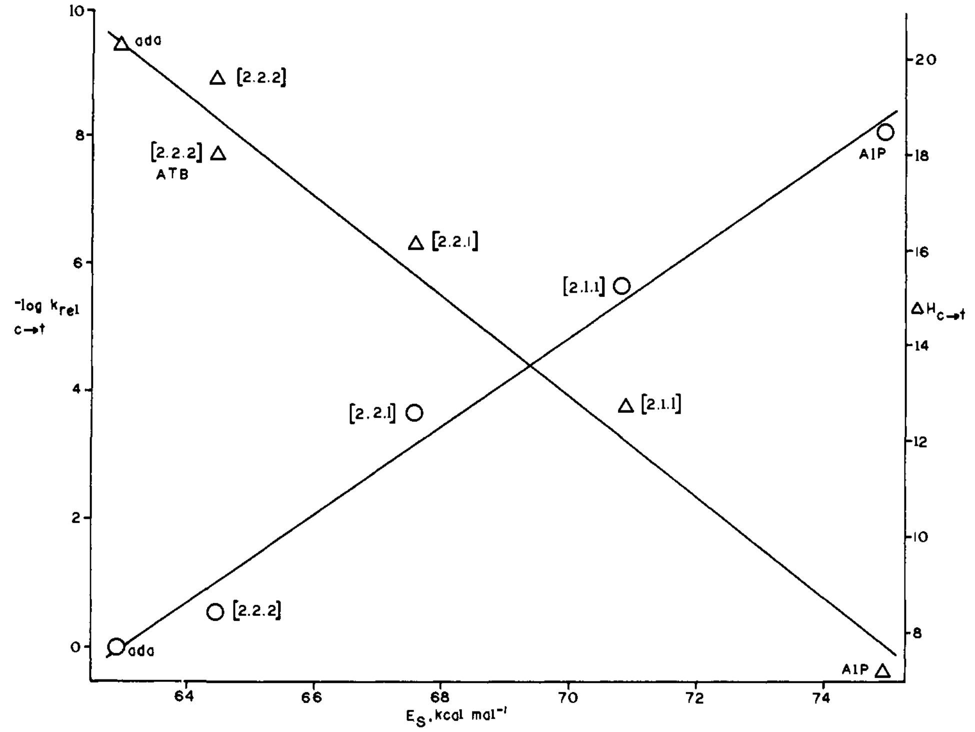

Figure 3. Log of the relative rate constant for cis → trans isomerization (Table V) vs. n,π* excitation energy (E_S, kcal mol^{-1}) of cis diazenes, (O) slope = 0.70 ± 0.04, intercept = −43.9 ± 2.7. Cis–trans ground state energy difference vs. E_S, (Δ) slope = −1.04 ± 0.08, intercept = 85.8 ± 5.1.

Table VII. Heat of Isomerization of Cis Diazenes

compd	ΔH_{isom}, kcal mol^{-1} [a]	ref
cis-[2.2.2]	18.0 ± 0.4	this work
cis-[2.2.1]	16.1 ± 0.5	this work
	18.8[b]	40
cis-[2.1.1]	12.7 ± 0.2[c]	this work
cis-azobenzene	11.7 ± 0.3[c]	this work
	10.0	41
	12.0	42
	11.52 ± 0.1	4, 43

[a] For solid cis going to solid trans. [b] In dodecane. [c] Derived from values in Table IX.

to measure ΔH_{isom} of *cis*-[2.2.2], an enormously more difficult experiment because this compound is so unstable thermally. Although reasonably consistent DSC results were obtained, we were unable to prove that the sample was pure cis. Analysis of *cis*-[2.2.1], *cis*-[2.1.1], and *cis*-azobenzene was conveniently carried out by HPLC, but injection of concentrated *cis*-[2.2.2] solutions onto an ice-cold silica gel column failed to produce a peak attributable to the cis isomer. Attempts to analyze *cis*-[2.2.2] by UV-visible spectroscopy were unsuccessful because ε of the impurity (trans) is 5 times smaller than ε of the major component. We showed that both isomers exhibited perfectly Gaussian absorption spectra, but a computer program designed to resolve the overlapping peaks failed to provide meaningful results. Nevertheless, the fact that *cis*-[2.2.2] was prepared in the same manner as pure *cis*-[2.2.1] and then handled rapidly in subdued light leads us to believe that the samples did not contain much trans.

Although ΔH_{isom} of solid cis going to solid trans was determined experimentally, ΔH_{isom} in nonpolar solvents is required for comparison with the other studies reported here. We did not measure heats of solution because earlier work on azobenzene[39] suggested that the two isomers would not differ significantly. According to Tables VII and IX, ΔH_{isom} for liquid *cis*-[2.1.1] is more negative than the solid phase value by 1.5 kcal mol^{-1} and ΔH_{isom} of *cis*-[2.2.1] in dodecane[40] is 2.7 kcal mol^{-1} more exothermic than our value. Even if these observations mean that the solid-phase isomerization heats are too low, a similar error would be introduced into all three diazenes. This would not change our conclusions; in fact, agreement in the case of *cis*-[2.2.2] would be improved (see Figure 4 and the Discussion section). For simplicity, we shall take the solid-phase values to be the same as ΔH_{isom} values in solution.

Discussion

The relative rates in Table V show that cis diazenes undergo thermal isomerization more slowly as the R group becomes smaller. The size of R also affects $\lambda_{\max}$(cis) because repulsion between R groups forces the nitrogen lone pairs into closer proximity, thus raising the energy of highest occupied nonbonding molecular orbital.[46] Since even the methyl groups in *cis*-dimethyldiazene are severely crowded,[47] this large steric effect is hardly surprising. It is remarkable, however, that there is linear correlation between the log of k_{rel}(cis → trans) (Table V) and the energy (kcal mol^{-1}) of the cis n,π* band (cf. Figure 3). The plot includes data for *cis*-azoisopropane (AIP), for which the $\lambda_{\max}$ value is 382 nm, $\Delta H^{\ddagger}_{\text{isom}}$ = 32.2 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = −4.4 eu.[7] Further discussion of this correlation will be found below.

Table VI compares deazatization rates of the three cis isomers which give at least some nitrogen. Since these rate constants are affected by solvent polarity (see below), we have listed k_{rel}(cis) in hexane. The value for *cis*-ATB was available in pentane[48] but

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[38] Engel, P. S.; Nalepa, C. J. *Pure Appl Chem.* **1980**, *52*, 2621. The activation parameters given for disappearance of *cis*-[2.2.1] in this reference are mistakenly those for *cis*-[2.1.1] (cf. Table I of the present paper).

[39] Haberfield, P.; Block, P. M.; Lux, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 5804.

[40] Schmittel, M.; Schulz, A.; Rüchardt, C.; Hädicke, E. *Chem. Ber.*, submitted for publication and private communication.

[41] Cole, L. G.; Gilbert, E. C. *J. Am. Chem. Soc.* **1951**, *73*, 5423; Corruccini, R. J.; Gilbert, E. C. *Ibid.* **1939**, *61*, 2925.

[42] Hartley, G. S. *J. Chem. Soc.* **1938**, 633.

[43] Wolf, E.; Cammenga, H. K. *Z. Phys. Chem.* **1977**, *107*, 21.

[44] Engel, P. S.; Wood, J. L.; Sweet, J. A.; Margrave, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 2381.

[45] Washburn, E. W., Ed.; "International Critical Tables"; McGraw-Hill, New York, 1929; Vol. 5, p 130.

[46] Baird, N. C.; deMayo, P.; Swenson, J. R.; Usselman, M. C. *J. Chem. Soc., Chem. Commun.* **1973**, 314.

[47] Stevens, J. F.; Curl, R. F.; Engel, P. S. *J. Phys. Chem.* **1979**, *83*, 1432.

Table VIII. Summary of Activation and Thermochemical Parameters[a] Used to Construct Figure 4

compd	$\Delta H^{\ddagger}_{\text{trans}\to\text{dec}}$	$\Delta S^{\ddagger}_{\text{trans}\to\text{dec}}$	$\Delta G^{\ddagger}_{\text{trans}\to\text{dec}}$	$\Delta H^{\ddagger}_{\text{isom}}$	$\Delta S^{\ddagger}_{\text{isom}}$	$\Delta G^{\ddagger}_{\text{isom}}$	$\Delta H^{\ddagger}_{\text{cis}\to\text{dec}}$	$\Delta S^{\ddagger}_{\text{cis}\to\text{dec}}$	$\Delta G^{\ddagger}_{\text{cis}\to\text{dec}}$	ΔH_{isom}
ada			42.7[b] (300)	23.2	3.0	22.3 (24.9)	28.5	20.5	22.4 (24.9)	
[2.2.2]			45.1[b] (300)	25.9	9.3	23.1 (33.1)			25.5 (33.1)	18.0
[2.2.1]	52.6[c]	3.2[c]	51.4 (381.1)	30.9	12.0	26.5 (90.7)				16.1
[2.1.1]				30.3	0.8	30.0 (141.6)				12.7
ATB	43.1[d]	17.0[d]	35.3 (183)				18.6[e]	5.3[e]	17.3 (−22)	
AIP	46.7[f]	14.1[f]	39.5 (315)	32.2[g]	−4.4[g]	34.0 (133)	39.9[g]	18.9[g]	32.2 (133)	

[a] Units are kcal mol^{-1} and eu. Temperatures shown (°C) are the mid-range values for each kinetic study and are used to calculate $\Delta G^{\ddagger}$. [b] Reference 13. [c] Reference 40. [d] Reference 6. [e] Reference 49. [f] Reference 51. [g] Reference 7.

Table IX. DSC Results

compd	sample wt, mg	process	ΔH, kcal mol^{-1}	av
cis-[2.2.2]	4.21	cis(s) → trans(s)	−18.77	−18.04
	5.06		−17.54	
	3.40		−17.81	
cis-[2.2.1]	4.00	cis(s) → trans(s)	−16.15	−16.11
	3.75		−17.74	
	4.89		−15.98	
	5.38		−16.67	
	5.03		−15.38	
	4.94		−14.72	
cis-[2.1.1]	3.39	cis(l) → trans(l)	−14.02	−14.19
	3.32		−14.47	
	3.04		−14.07	
cis-[2.1.1]	3.39	cis(s) → cis(l)	3.57	3.70
	3.32		3.74	
	3.04		3.78	
trans-[2.1.1]	4.64	trans(s) → trans(l)	2.21	2.21
	3.40		2.30	
	3.11		2.13	
trans-[2.2.2]	6.29	trans(s) → trans(l)	4.74	
trans-[2.2.1]	4.57	trans(s) → trans(l)	3.54	3.57
	4.71		3.60	
trans-[2.2.1]		trans(s) → trans(g)	18.8[a]	
cis-azobenzene	1.95	cis(s) → trans(l)	−6.24	−6.61
	5.79		−7.06	
	3.32		−6.53	
trans-azobenzene	6.25	trans(s) → trans(l)	4.75	5.08[b]
	5.31		5.19	
	5.05		5.29	
benzoic acid	1.43	(s) → (l)	4.13[c]	
naphthalene	2.36	(s) → (l)	4.48[d]	

[a] Carried out by UV spectroscopy; cf. ref 44. [b] Literature[45] value 5.42. [c] Literature[45] value 4.14. [d] Literature[45] value 4.49.

the others had to be interpolated from data in other solvents.[49] It will be noted that replacing the *tert*-butyl groups by adamantyl or bicyclooctyl moieties slows down decomposition by roughly equal amounts in both the cis and trans series. This is attributable to differences in radical stability and the requirement for planarity at the transition state for homolysis.[13,19,20] In addition, the rate of nitrogen loss is strongly influenced by cis ground state energy. As an extreme example, *trans*-ATB decomposes 63 times faster than *trans*-AIP, but *cis*-ATB decomposes 3 × 10^{12} faster than *cis*-AIP. The observation that k_{rel} for *cis*-[2.2.2] is 10 times slower than k_{rel} for *trans*-[2.2.2] suggests that the cis ground state may lie slightly lower than that of *cis*-ATB or *cis*-ada. This supposition is in accord with the smaller steric requirement of the bicyclo[2.2.2]octyl group than the other two groups.[18]

A complete understanding of diazene thermal chemistry requires that we know the energy of all starting materials and transition states for decomposition and isomerization. The available data (Table VIII) allow us to construct energy diagrams (Figure 4) which explain cis diazene thermal chemistry in a concise and self-consistent manner. The trans isomer of each diazene in Figure 4 is arbitrarily set as the zero of energy. Because of the large temperature range spanned in these studies, the variations in $\Delta S^{\ddagger}$, and the unavailability of some activation parameters, we have employed free energies ($\Delta G^{\ddagger}$)[50] determined at the temperature

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(48) Schulz, A.; Rüchardt, C. *Tetrahedron Lett.* **1976**, 3883.

(49) From Table IV, $k_{\text{dec}}(\phi CH_3, 26\ °C) = 3.10 \times 10^{-4}\ s^{-1}$. From Tables I and II, $k_{\text{dec}}(i\text{-PrOH}, 26\ °C) = 3.69 \times 10^{-4} \times 0.13 = 4.80 \times 10^{-5}\ s^{-1}$. If log k_{dec} is proportional to the solvent parameter E_T, one can extrapolate these data to hexane as follows: $[(48.6 - 33.9)/(48.6 - 30.9)] = [(-4.319 + 3.509)/(-4.319 - \log k_{\text{dec}}(\text{hexane}))]$. This gives $k_{\text{dec}}(\text{hexane}, 26\ °C) = 4.53 \times 10^{-4}\ s^{-1}$. The value for k_{rel} of *cis*-[2.2.2] was deduced as follows. Interpolation of the data in Table I yields $k_{\text{dis}}(\phi CH_3, 25\ °C) = 6.90 \times 10^{-5}\ s^{-1}$. Since most of the [2.2.2] undergoes isomerization in both toluene and hexane, we shall assume that k_{dis} (disappearance) behaves the same as for *cis*-[2.2.1]; namely, it is 34% faster in hexane. (The [2.2.2] was actually done in dodecane and xylene). In hexane, 11% of the *cis*-[2.2.2] was found to decompose at 25 °C, so that $k_{\text{dec}} = 6.90 \times 10^{-5} \times 1.34 \times 0.11 = 1.02 \times 10^{-5}\ s^{-1}$.

(50) Trost, B. M.; Scudder, P. H. *J. Org. Chem.* **1981**, *46*, 507, and ref 15 and 16 cited therein.

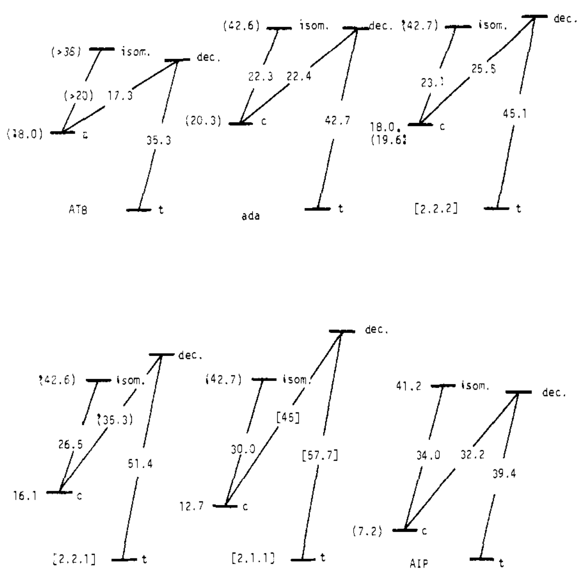

Figure 4. Energy diagram for 1,2-diazenes. The trans ground state is taken as the energy zero. Measured values are unmarked, derived values are in parentheses, and estimated values are in brackets.

of each kinetic study (included in Table VIII). The errors introduced by this procedure are certainly no greater than those inherent in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ measurements.

There are two ways of deducing the energy of cis diazenes relative to their trans isomers: (a) subtracting $\Delta G^\ddagger$ for decomposition of cis from $\Delta G^\ddagger$ for decomposition of trans and (b) direct measurement of ΔH_{isom}, in this case by DSC. Because *cis*-ATB leads exclusively to nitrogen, only the substraction method is applicable to this compound. *cis*-[2.2.1] and *cis*-[2.1.1], on the other hand, produce the trans isomer quantitatively on heating so that only the DSC method can give the cis energy. Since the substraction of $\Delta G^\ddagger$'s assumes that the two isomers decompose by isoenergetic transition states, it is important to test this assumption by applying both methods to the same compound. The only viable candidates for such a comparison are *cis*-ada and *cis*-[2.2.2], but DSC studies on the former are impractical because of its instability and because the measured reaction enthalpy will correspond to some combination of decomposition and isomerization. As described above, we were able to obtain ΔH_{isom} of *cis*-[2.2.2] by DSC, since the dominant reaction by far is isomerization. There is just enough decomposition, however, to allow an estimate of $\Delta G^\ddagger$ for this process. Thus the rate constant for disappearance of *cis*-[2.2.2] (Table I) multiplied by the fraction which decomposes (Table V) gives a rate constant for nitrogen loss which corresponds to $\Delta G^\ddagger = 25.5$ kcal mol^{-1}. Subtracting this value from the 45.1 kcal mol^{-1} for decomposition of *trans*-[2.2.2], we obtain a difference of 19.6 kcal mol^{-1}, which compares favorably with the DSC ΔH_{isom} of 18.0 kcal mol^{-1}. It is true that enthalpies cannot strictly be compared with free energies, but the entropy of cis and trans diazenes is not likely to differ substantially.

The energies of the cis diazenes studied here (Figure 4) are considerably higher than most of those calculated for cis diimide or *cis*-azomethane.[6] Clearly, steric repulsion between bulky groups raises the ground-state energy. This repulsion also forces the antisymmetric combination of n orbitals (n_-) into closer proximity, raising the HOMO and lowering the singlet excitation energy (E_S). As seen in Figure 3, the cis–trans energy gap [which determines log k_{rel}(cis → trans)] correlates remarkably well with E_S, giving a slope of -1. This observation is most simply explained if R groups of varying bulk affect only the energy of the n_- orbital, which in turn governs both E_S and the total energy of cis diazene. More likely, the nature of R affects several of the MO's, but those other than n_- may vary in such a way as to leave the total energy nearly unchanged. There is some evidence that variations in n_- orbital energy account for much of the cis–trans enthalpy difference in that the lowest ionization potential (IP) of *cis*-AIP is 5.3 kcal mol^{-1} below that of *trans*-AIP,[52] while the ground-state energy difference is calculated to be 7.2 kcal mol^{-1} (cf. Figure 4). Although there is only a rough correlation between the n_- IP and E_S for diazenes,[52] photoelectron spectroscopy on the present closely related compounds might well reveal a linear relationship between these quantities and ΔH_{isom}. Since the required data are presently lacking, we can admire only qualitatively the enormous influence which the nitrogen lone pairs exert on both the thermal and spectroscopic properties of cis diazenes.

Experimental ΔH_{isom}'s for all of the diazenes would certainly be useful; in fact, we tried to obtain such data by catalyzing conversion of cis to trans. If a suitable catalyst were found for *cis*-[2.2.2], it could be applied in a solution calorimeter to the unstable compounds such as *cis*-ATB and *cis*-ada. We tried various acids[9] and transition-metal complexes[3] but none possessed the necessary characteristics of rapidity and cleanness.

Although this unfortunate circumstance might well be rectified by further research, our ignorance is presently greatest for ATB, the most common diazene in Figure 4. *cis*-ATB exhibits no detectable reversion to trans; hence, one can only guess where the isomerization transition state lies. The value >38 kcal mol^{-1} was deduced by assuming that <1% of *cis*-ATB gives trans, but even this figure is questionable because the low ϵ of trans relative to cis makes UV spectral analysis difficult. The correlation between E_S and log k_{rel} for isomerization shown in Figure 3 can be used to arrive at a value for $\Delta G^\ddagger_{\text{isom}}$ of *cis*-ATB. The $\lambda_{\max}$ of 445 nm ($E_S = 64.3$ kcal mol^{-1}) corresponds to $k_{\text{rel}} = 0.1$ and $k = 2.84 \times 10^{-5}$ s^{-1} at 25 °C (Table IV). This in turn leads to $\Delta G^\ddagger_{\text{isom}} = 23.6$ kcal mol^{-1} and an isomerization transition state energy of 41.6 kcal mol^{-1}, entirely consistent with Figure 4. It is also encouraging to note that a force field calculation[53] on ATB resulted in a cis–trans energy difference of 20.9 kcal mol^{-1}, in reasonable agreement with the derived value of 18.0 kcal mol^{-1}.

The relative position of the two transition states in Figure 4 shows why some cis diazenes decompose to nitrogen and others isomerize to trans. *cis*-Ada is particularly interesting because it undergoes both processes simultaneously. According to Table IV, decomposition of *cis*-ada possesses both a higher $\Delta H^\ddagger$ and $\Delta S^\ddagger$ than isomerization. Precisely the same behavior has been noted[7] for *cis*-AIP, as indicated in Table VIII. Low values of $\Delta S^\ddagger$ for isomerization have also been observed for *cis*-phenylazo-*tert*-butane[54] ($\Delta S^\ddagger = 0$–3.6 eu) and *cis*-aryldiazenes ($\Delta S^\ddagger = -7$–11 eu).[2] Some diazenes can isomerize without giving a low $\Delta S^\ddagger$ value, as seen in Table I for *cis*-[2.2.1] and *cis*-[2.2.2]. Since Rüchardt and co-workers obtained $\Delta H^\ddagger = 27.8$ kcal mol^{-1} and $\Delta S^\ddagger = 1.9$ eu for *cis*-[2.2.1] in dodecane,[40] one might question our high $\Delta S^\ddagger$ values. However, the fact that activation entropies differ so much from one laboratory to another emphasizes the danger of mechanistic conclusions based solely on this parameter.

The mechanism by which cis diazenes isomerize thermally to trans is a subject of controversy.[39,43,55] Although theorists[56] clearly favor inversion of one R group through a nitrogen atom (semilinearization) over the alternative rotation about the N=N bond, meaningful experiments to rule out one or the other mechanism are not readily conceived. A key observation about Figure 4 affords us an opportunity to evaluate these mechanisms; namely,

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(51) Perona, M. J.; Beadle, P. C.; Golden, D. M. *Int. J. Chem. Kinet.* **1973**, *5*, 495.

(52) Houk, K. N.; Chang, Y. M.; Engel, P. S. *J. Am. Chem. Soc.* **1975**, *97*, 1824.

(53) Kao, J.; Huang, T. N. *J. Am. Chem. Soc.* **1979**, *101*, 5546.

(54) Porter, N. A.; Funk, M. O. *J. Chem. Soc., Chem. Commun.* **1973**, 263.

(55) (a) Llunggren, S.; Wettermark, G. *Acta Chem. Scand.* **1971**, *25*, 1599; (b) Wildes, P. D.; Pacifici, J. G.; Irick, G.; Whitten, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 2004; (c) Nerbonne, J. M.; Weiss, R. G. *Ibid.* **1978**, *100*, 5953; (d) Asano, T. *Ibid.* **1980**, *102*, 1205; (e) Nishimura, N.; Sueyoshi, T.; Yamanaka, H.; Imai, E., Yamamoto, S.; Hasegawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1381.

(56) (a) Baird, N. C.; Swenson, J. R. *Can. J. Chem.* **1973**, *51*, 3097; (b) Camp, R. N.; Epstein, I. R.; Steel, C. *J. Am. Chem. Soc.* **1977**, *99*, 2453; (c) Kearns, D. R. *J. Phys. Chem.* **1965**, *69*, 1062; (d) Howell, J. M.; Kirschenbaum, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 877; (e) Gordon, M. E.; Fischer, H. *Ibid.* **1968**, *90*, 2471; (f) Winter, N. M.; Pitzer, R. M. *J. Chem. Phys.* **1975**, *62*, 1269; (g) Olbrich, G. *Chem. Phys.* **1978**, *27*, 117; (h) Pasto, D. J.; Chipman, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 2290.

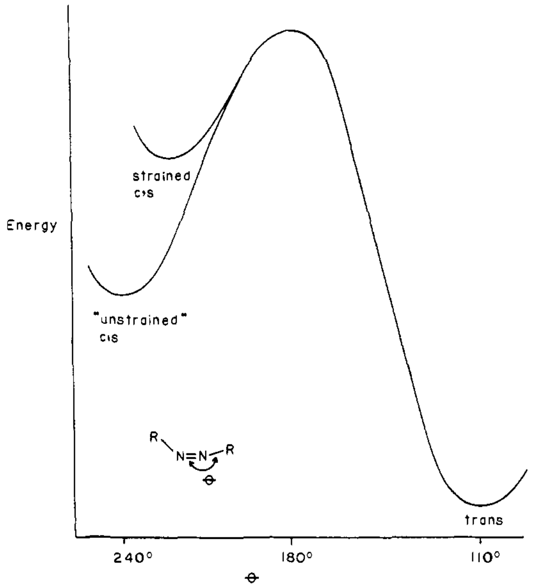


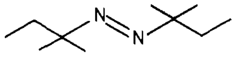
Figure 5. Potential energy diagram for isomerization of cis diazenes by the semilinearization mechanism.

the isomerization transition state occurs at 42 ± 1 kcal mol^{-1} regargless of cis diazene energy. This barrier falls into the range calculated for inversion (37–66 kcal mol^{-1}) but below that calculated for rotation (59–84 kcal mol^{-1}).[56] A second argument is based on the predicted effect of steric size on the two possible mechanisms. By analogy with olefins,[57] introduction of bulky substituents is expected to open the N=N—C angles without twisting the N=N π bond. The potential surface for twisting of a diazene[46] is no less steep than that for a carbon–carbon double bond. Moreover, *cis*-azomethane remains planar despite crowding of the methyl groups[47] and *cis*-[2.2.1] has a C–N=N–C dihedral angle of only 3°. This figure is derived from a very recent X-ray crystal structure[40] which further revealed an unusually large C–N=N angle of 129.3° in *cis*-[2.2.1].[58] It follows that bulky R groups move the diazene along the reaction coordinate for isomerization by the inversion mechanism but not along the pathway for N=N twisting. Since cis diazenes are essentially planar, the inversion mechanism explains why raising the cis ground state energy lowers $\Delta G^{\ddagger}$ for isomerization by an equal amount. This sort of reasoning has been used previously in discussing the rotational barrier for disulfides.[59]

Figure 5 shows how the potential curves might look for a low and a high energy cis diazene. Theoretical calculations[56] place the peak at 180°, a value which should certainly be independent of structure. Incorporated into Figure 5 are the experimental facts that the transition-state energy is constant and that the C–N=N angle opens as R becomes bulkier. Although the Hammond postulate[60] applies strictly to high-energy intermediates and the transition states leading to them, it is amusing to consider Figure 5 in these terms. The structure of the transition state more closely resembles that of starting material when reactivity increases; however, it is the starting cis diazene and not the transition state whose location varies along the reaction coordinate.

Before leaving the subject of diazene isomerization mechanisms, it is worthwhile to consider the possibility that the trans diazene is produced by C–N scission followed by alkyl–diazenyl recombination (k_4, k_7 in Scheme I). We can rule out this mechanism for *cis*-[2.2.1] because the 1-norbornyldiazenyl radical is known[12] to lose nitrogen. Since no nitrogen is evolved on heating *cis*-[2.2.1], this diazenyl radical, and very likely the one from *cis*-[2.1.1], does not lie on the isomerization pathway. On the other hand, the scission–recombination mechanism does hold for certain arylalkyldiazenes[11] and is not easily dismissed for *cis*-ada and *cis*-[2.2.2]. Attempts to observe CIDNP during thermolysis of *cis*-ada gave negative results. Because the inversion mechanism is entirely consistent with our data, we see no reason to invoke scission–recombination as an important pathway for isomerization of the diazenes studied here.

Large solvent effects on decomposition rates of diazenes have been observed previously. Whereas compounds **19**[61] and **20**[62] show essentially no solvent effect. *cis*-ATB decomposes 50 times faster in pentane than in methanol.[48] Thermolysis of cyclic diazenes, e.g., **21**, is also sensitive to solvent polarity. Since these effects are peculiar to the more polar[47] cis diazene linkage, they have been interpreted as ground-state solvation which is lost in the transition state. Schulz and Rüchardt obtained an excellent correlation[48] between the thermolysis rate of *cis*-ATB and the solvent polarity parameter E_T, the slope being −0.071 ± 0.002. The same group[40] found later that isomerization of *cis*-[2.2.1] is much less sensitive to solvent polarity, the slope in this case being only −0.034 ± 0.003. Since *cis*-ada undergoes two competing processes, one expects from these results that polar solvents would inhibit decomposition more than isomerization. That this is the case is apparent from Table II. An attempt to correlate log (dec/isom) with E_T gave a line of slope −0.055 if the value for acetone was omitted. Although many solvents were tried, solubility problems and the growth of an interfering short-wavelength UV band prevented us from carrying out a complete solvent study. Since even the data for acetone were only marginally acceptable and alcohols give anomalously fast isomerization rates,[40] quantitative evaluation of solvent effects on *cis*-ada is not possible. We know from the *cis*-ATB results that cis ground states are solvated; hence, the relative insensitivity of isomerization rates to solvent polarity suggests that the isomerization transition state is nearly as polar as the ground state.



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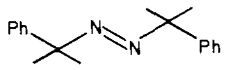
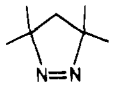


20



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Thermolysis rates of cis diazenes are very much faster than those of trans diazenes because of the energy "locked" into the former. It is therefore possible to generate bridgehead free radicals under mild conditions from *cis*-ada and *cis*-[2.2.2]. Because very little is known about the products of such radicals,[63] work along these lines is in progress.

In summary, we have shown that cis diazenes can isomerize thermally to trans, decompose to nitrogen, or undergo both reactions simultaneously. Bulky R groups force the nitrogen lone pairs into closer proximity, thereby raising the cis ground state energy and decreasing the singlet excitation energy by the same amount. Cis diazenes can be very stable thermally if the attached alkyl groups are small and are highly unfavorable as free radicals. Finally, the general shape of the potential energy curve for isomerization has been deduced.

Experimental Section

Synthesis of Trans Bicyclic Diazenes. The trans diazenes were prepared from the corresponding sulfamides by the Stowell[21] modification of the Ohme, Preuschhof, Heyne procedure. Yields are for 1–3-g quantities.

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(57) Even *cis*-di-*tert*-butylethylene is nearly planar: Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121.

(58) The 129.3° angle in *cis*-[2.2.1] makes it unlikely that *cis*-AIP has a still larger angle[52] in view of the greater steric requirement of 1-norbornyl than isopropyl.[18]

(59) Jorgensen, F. S.; Snyder, J. P. *Tetrahedron* **1979**, *35*, 1399.

(60) (a) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334; (b) Farcasiu, D. *J. Chem. Educ.* **1975**, *52*, 76.

(61) Duismann, W.; Rωdduchardt, C. *Chem. Ber.* **1978**, *111*, 596.

(62) Timberlake, J. W., unpublished results.

(63) Some product data for perester thermolysis in cumene can be found in ref 27 and 64.

trans-Bis(1-adamantyl)diazene was obtained in 80% yield after chromatography (silica gel) and sublimation [120 °C (0.1 mm)]: mp 280–285 °C (lit.[65] mp 280–284 °C).

trans-Bis(1-bicyclo[2.2.2]octyl)diazene was obtained in 92% yield (crude) and was purified by chromatography (silica gel) and recrystallization (ethanol): mp 132–134 °C (lit.[13] mp 133–134 °C).

trans-Bis(norbornyl)diazene was obtained in 95% yield (crude) and was recrystallized from methanol: mp 166–167 °C (lit.[13] mp 164 °C).

trans-Bis(bicyclo[2.1.1]hexyl)diazene (0.93 g from 2.02 g of sulfamide) was obtained in 62% yield after chromatography (silica gel-hexane–benzene, 1:1) and recrystallization from methanol: mp 117.5–119 °C; NMR (CCl_4) δ 2.39 (br s, 1 H), 1.9–1.4 (m, 8 H); UV λ_{max} (hexane) 370 nm (ϵ 21).

Anal. Calcd $C_{12}H_{18}N_2$: C, 75.74; H, 9.53; N, 14.72. Found: C, 75.93; H, 9.53; N, 14.62.

If the above chromatography was continued using ether as an eluant, a 22% yield, after sublimation (0.33 g from 2.02 g of sulfamide), of the cis diazene was obtained; cf. irradiation of trans for identification.

Synthesis of *N*,*N*′-Bis(bicycloalkyl)sulfamides. The sulfamides were all prepared by addition of amine to a cold (−50 °C) methylene chloride or hexane solution of dry triethylamine or pyridine and distilled sulfuryl chloride. The free amines were found to form carbonates on standing in air and were therefore used directly after liberation from the corresponding HCl salts with a carbonate-free 10% sodium hydroxide solution. The latter was prepared by treating the NaOH solution with $BaCl_2$ and filtering prior to use.

***N*,*N*′-Bis(1-adamantyl)sulfamide.** From 3.0 g (0.02 mol) of 1-aminoadamantane, 3.0 g (0.03 mol) of triethylamine and 1.48 g (0.011 mol) of sulfuryl chloride was obtained 1.6 g (88%) of crude sulfamide. The sulfamide was extracted with benzene to remove an unknown impurity and recrystallized from ethanol to give a 35% yield: mp 247–249.5 °C (lit.[13] mp 239 °C).

***N*,*N*′-Bis(1-bicyclo[2.2.2]octyl)sulfamide.** From 1.88 g (15 mmol) of liberated 1-aminobicyclo[2.2.2]octane, 1.42 g (15 mmol) of triethylamine, and 1.01 g (7.5 mmol) of sulfuryl chloride in hexane was obtained after recrystallization from hexane 0.85 g (32%) of pure sulfamide: mp 185–187 °C (lit.[13] mp 188 °C).

***N*,*N*′-Bis(1-norbornyl)sulfamide.** From 2.22 g (20 mmol) of 1-aminobicyclo[2.2.1]heptane, 2.02 g (20 mmol) of triethylamine, and 1.35 g of $CHCl_3$–hexane, 1.36 g (47%) of pure sulfamide: mp 179–180 °C (lit.[13] mp 176–178 °C).

***N*,*N*′-Bis(1-bicyclo[2.1.1]hexyl)sulfamide.** From 2.26 g (23.5 mmol) of liberated amine, 2.38 g (23.5 mmol) of triethylamine, and 1.59 g (11.8 mmol) of sulfuryl chloride in hexane was obtained after recrystallization 2.02 g (67%) of sulfamide: mp 197–200 °C. Recrystallization from benzene gave an analytical sample: mp 199.5–201 °C.

Anal. Calcd $C_{12}H_{20}N_2O_2S$: C, 56.22, H, 7.86; N, 10.93. Found: C, 56.52; H, 7.85; N, 11.00.

Synthesis of Bicyclic Amines. 1-Aminobicyclo[2.2.1]heptane was obtained from the carboxylic acid[13,23,24] by the Schmidt reaction as described by Rüchardt.[13]

1-Aminobicyclic[2.2.2]octane. Bicyclo[2.2.1]heptyl-1-carbinol was prepared from norbornanecarboxylic acid by reduction with lithium aluminum hydride, mp 60–62 °C after sublimation (lit.[66] mp 63–63.4 °C). This alcohol was converted to amide and hydrolyzed to the amine as follows. To a mixture of 50 mL of concentrated sulfuric acid and 45 mL of 30% fuming sulfuric at 0 °C, was added 3.0 mL of acetonitrile. An ice-cooled solution of 4.3 g (34 mmol) of bicyclo[2.2.1]heptyl-1-carbinol in 25 mL of acetonitrile was added dropwise. The solution was stirred 2.5 h at 0 °C and poured into 1000 mL of ice water. After the solution was neutralized with sodium carbonate, it was extracted with 4 × 1000 mL of ether. The ether was dried ($MgSO_4$) and concentrated to yield 4.8 g (85% crude) *N*-bicyclo[2.2.2]octylacetamide: mp 130–131 °C (petroleum ether) (lit.[25] mp 135–136 °C).

A solution of 5.0 g (30 mmol) of this acetamide in 75 mL of concentrated HCl was stirred at reflux for 2 days. The reaction mixture was washed with 2 × 50 mL of ether and the aqueous acid was concentrated in vacuo to yield 4.74 g of crude solid which was recrystallized from ethanol–ether, mp >350 °C (lit.[25] mp >350 °C).

1-Aminobicyclo[2.1.1]hexane was prepared by the scheme shown in the text. Two methods were employed for preparation of the key intermediate, 3-methylene-1,6-heptadiene (12).

Method A. Addition of Copper–Grignard Reagent to Vinylacetylene. To 3.04 g (0.125 mol) of magnesium suspended in 20 mL of dried THF was added 17.5 g (0.13 mmol) of 4-bromo-1-butene in 200 mL of THF. After formation (1 h), the Grignard reagent was separated from unreacted Mg by filtering through glass wool under a nitrogen atmosphere directly into a second reaction flask. Anhydrous cuprous bromide (9.1 g, 63 mmol) was added to the Grignard reagent cooled to −50 °C. A xylene–vinylacetylene solution (Chemical Samples Co., ~20 mL of 50% by weight) was added by syringe to a flask connected by a distillation head to a graduated receiver cooled to −80 °C. Under a nitrogen stream, the flask was heated to 60 °C until 3.8 mL of vinylacetylene was trapped. The vinylacetylene was distilled directly into the copper–Grignard reagent at −50 °C and the reaction was allowed to stir for 20 min at −25 °C. The mixture was poured into ice water, and 9.5 g of NaCN and 13 g of NH_4Cl were added. The aqueous solution was extracted with low boiling petroleum ether, and the organic extracts were washed repeatedly with water. After drying (Na_2SO_4) and removal of he solvent, the residue was chromatographed (neutral alumina, eluant pentane) to give 2.71 g (39%) of the triene of ~90% purity by GC.

Method B. 3-Methylene-1,6-heptadiene was prepared essentially according to Kawamura et al.[67] 3-Methyl-2,5-dihydrothiophene 1,1-dioxide was prepared in 89% yield[68] and converted to 3-bromomethyl-2,5-dihydrothiophene 1,1-dioxide in 38% yield,[69] which was in turn pyrolyzed to 2-bromomethyl-1,3-butadiene in 50% yield. An attempt to prepare the latter by direct bromination of isoprene with NBS failed. The bromobutadiene was reacted with 2 equiv of allylmagnesium bromide in ether for 4 h at 5 °C according to the literature[67] to give a 68% yield of 3-methylene-1,6-heptadiene.

1-Vinylbicyclo[2.1.1]hexane was prepared in 41% yield from the photochemical cyclization of 3-methylene-1,6-heptadiene.[29] The best yield was obtained by irradiation of a 1% solution of triene (3.5 g/350 mL) in the presence of 4% of β-acetonaphthone for 25 h with a 450-W Hanovia lamp in a quartz reactor. The reaction progress was monitored by GC (10 ft, 10% Carbowax column at 70 °C).

Bicyclo[2.1.1]hexane-1-carboxylic acid was prepared according to the literature[67] in 67% yield: after sublimation, mp 50–51 °C (lit.[29] mp 46–50 °C).

The acid was converted into the amine by the Schmidt reaction as described previously.[29] The amine was isolated as the HCl salt in 60% yield and was used to make the sulfamide without further purification.

Synthesis of Cis Bicyclic Diazenes. In all cases the cis diazenes were generated by irradiation in solution of the corresponding trans isomers in a Rayonet reactor at 350 nm or with a 500-W short-arc mercury lamp and a Corning 7-54 filter.

***cis*-1-Norbornyldiazene** was isolated in pure form by column chromatography on basic alumina (ethyl acetate) and recrystallization from pentane: mp 92–93 °C; UV λ_{max} 423 nm (ϵ 123).

***cis*-Bicyclo[2.1.1]hexyldiazene** was isolated by chromatography on Florisil. The unisomerized trans eluted first (hexane–ether, 3:1) followed by cis (hexane–ether, 1:1). From 0.30 g of trans was isolated 0.20 g (67%) of starting material and 0.099 g (33%) of cis, which was sublimed and recrystallized from hexane: mp 89–90 °C; UV λ_{max} 404 nm (ϵ 118); NMR ($CDCl_3$) δ 2.45 (br s, 1 H), 2.05–1.45 (m, 8 H). Irradiation beyond 24 h caused no apparent change in the ratio of trans:cis (~2:1), presumably because the photostationary state had been reached.

***cis*-Bicyclo[2.2.2]octyldiazene** precipitated spontaneously upon irradiation of the trans isomer in pentane. Due to the lability of this compound, it was characterized only by UV and by its behavior on the DSC.

Kinetics. Degassed, sealed solutions of trans diazenes in xylene were irradiated in square cuvettes at 0 °C, using light from a 500-W high-pressure mercury lamp and a Corning 7-54 filter. The cuvettes containing the yellow cis isomers were plunged into a small stirred oil bath in the cell compartment of a Cary 17 spectrometer. Temperature was regulated by a Bayley controller and was monitored continuously with a Minco platinum thermometer, Leeds and Northrup K-5 potentiometer, and chart recorder. The absorbance of cis was followed until it ceased to change, and the data were fit by computer to a first-order plot. It was necessary to add a drop of triethylamine or solid potassium carbonate to the solutions; otherwise nonlinear and irreproducible results were obtained, presumably because of adventitious acid-catalyzed isomerization.

Differential Scanning Calorimetry was carried out on a DuPont Model 990 thermal analyzer using high-purity indium as a standard. Samples were hermetically sealed into aluminum pans. The DSC was interfaced to a PDP 11/70 computer, producing data files which were analyzed on a Hewlett Packard Model 2648A graphics terminal. The isomerization enthalpy of *cis*-[2.2.1] and *cis*-[2.2.2] was obtained directly from the peak

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[64] Lorand, J. P.; Chodroff, S. D.; Wallace, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 5266.

[65] Prochazka, M.; Ryba, O.; Lim, P. *Collect. Czech. Chem. Commun.* **1968**, *33*, 3387.

[66] Applequist, D. E.; Kaplan, L. *J. Am. Chem.* Soc. **1965**, *87*, 2194.

[67] Kawamura, T.; Matsunaga, M.; Yonezawa, T. *J. Am. Chem. Soc.* **1978**, *100*, 92.

[68] Frank, R. L.; Seven, R. P. "Organic Synthesis", Collect. Vol. 3; Wiley: New York, 1960; p 499.

[69] Krug, R. C.; Yen, T. F. *J. Org. Chem.* **1956**, *21*, 1082.

areas, but the low melting point of *cis*-[2.1.1] and *cis*-azobenzene necessitated correcting for the heat of fusion of one or both isomers. Thus for *cis*-[2.1.1], $\Delta H(\text{cis,s} \rightarrow \text{trans,s}) = \Delta H(\text{cis,l} \rightarrow \text{trans,l}) + \Delta H(\text{cis,s} \rightarrow \text{cis,l}) - \Delta H(\text{trans,s} \rightarrow \text{trans,l})$. Darkening of the *cis*-[2.1.1] samples was noticed when the pans were opened after the DSC runs. However, the fact that the preisomerization base line extrapolates to the postisomerization base line speaks for the absence of deep-seated decomposition.

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"Spontaneous" Formation of Radicals from Nitroso Compounds. Inadvertent Photolysis vs. Molecule Assisted Homolysis[1]

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Abstract: The formation of radicals by a "spontaneous" reaction between nitroso compounds and certain organic materials has often been reported in the literature and has generally been ascribed to a process of molecule assisted homolysis (MAH). Some selected "spontaneous" radical-forming processes involving trifluoronitrosomethane, nitrosobenzene, and 2,4,6-trichloronitrosobenzene have been reexamined. In many cases it has been found that the radicals are formed only when the sample is exposed to ordinary laboratory light. It is suggested that the role of light on other "spontaneous" radical-forming reactions should be investigated.

Introduction

Pryor and co-workers[3] have identified three types of polymolecular process by which radicals are produced from the interaction of closed-shell (i.e., singlet) molecules. These are: molecule assisted homolysis (MAH), in which acceleration of a single bond homolysis is caused by the interaction of one molecule with another; interactions of two π systems leading to diradicals; and one-electron transfer reactions in which a donor and an acceptor exchange an electron to produce two radicals or radical ions.[4] The mechanisms of many such processes are still not firmly established. Particularly intriguing is the "spontaneous" formation of free radicals which has often been observed when nitroso compounds are mixed with other organic compounds at ambient temperatures.[5-23] These reactions have been studied by EPR spectroscopy.[24,25] With certain exceptions the radicals have been correctly identified as nitroxides, though not all the nitroxides have had

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(1) Issued as N.R.C.C. No. 19555.

(2) N.R.C.C. Research Associate, 1979-80.

(3) Pryor, W. A.; Coco, J. H.; Daley, W. H.; Houk, K. N. *J. Am. Chem. Soc.* **1974**, *96*, 5591. Pryor, W. A. *ACS Sym. Ser.* No. 69 **1978**, 33.

(4) (a) The term "molecule induced radical formation", MIRF, which has been used to describe all three processes, seems to have fallen into disuse. (b) Hamony, J. A. K. *Methods Free-Radical Chem.* **1974**, *5*, 101.

(5) A comprehensive literature search was not attempted. The references cited below[6-22] related primarily to radical formation from CF_3NO,[6,7] nitrosobenzene and other aromatic nitroso compounds,[6d,8-21] and $(CH_3)_3CNO$.[14,15,22]

(6) (a) Ginsburg, V. A.; Dubov, S. S.; Medvedev, A. N.; Martynova, L. L.; Tetel'baum, B. I.; Vasil'eva, M. N.; Yakubovich, A. Ya. *Dokl. Akad. Nauk SSSR* **1963**, *152*, 1104. (b) Ginsburg, V. A.; Medvedev, A. N.; Lebedeva, M. F.; Dubov, S. S.; Yakubovich, A. Ya. *Zh. Obshch. Khim.* **1965**, *35*, 1418. (c) Ginsburg, V. A.; Medvedev, A. N.; Martynova, L. L.; Vasil'eva, M. N.; Lebedeva, M. F.; Dubov, S. S.; Yakubovich, A. Ya. *Ibid.* **1965**, *35*, 1924. (d) Ginsburg, V. A.; Medvedev, A. N.; Dubov, S. S.; Lebedeva, M. F. *Ibid.* **1967**, *37*, 601. (e) Ginsburg, V. A.; Mededev, A. N.; Lebedeva, M. F.; Vasil'eva, M. N.; Martynova, L. L. *Ibid.* **1967**, *37*, 611. (f) Ginsburg, V. A.; Medvedev, A. N.; Miszabekova, N. S.; Lebedeva, M. F. *Ibid.* **1967**, *37*, 620. (g) Medvedev, A. N.; Smirnov, K. N.; Dubov, S. S.; Ginsburg, V. A. *Ibid.* **1968**, *38*, 2462. (h) Ginsburg, V. A.; Medvedev, A. N.; Dubov, S. S.; Gitel', P. O.; Smolyanitskaya, V. V.; Nikolaenko, G. E. *Ibid.* **1969**, *39*, 282. (i) Ginsburg, V. A.; Smolyanitskaya, V. V.; Medvedev, A. N.; Faermark, V. S.; Tomilov, A. P. *Ibid.* **1971**, *41*, 2284. (j) Ginsburg, V. A.; Medvedev, A. N.; Martynova, L. L.; Gitel', P. O.; Nikolaenko, G. E. *Zh. Org. Khim.* **1972**, *8*, 486. (k) Ginsburg, V. A.; Medvedev, A. N.; Gitel', P. O.; Lagutina, Z. N.; Martynova, L. L.; Lebedeva, M. F.; Dubov, S. S. *Ibid.* **1972**, *8*, 500. (l) Ginsburg, V. A.; Medvedev, A. N.; Lebedev, M. F.; Martynova, L .L. *Ibid.* **1974**, *10*, 1416, and other works by the same authors cited in the foregoing papers.

(7) Booth, B. L.; Edge, D. J.; Haszeldine, R. N.; Holmes, R. G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 7.

(8) Sullivan, A. B. *J. Org. Chem.* **1966**, *31*, 2811.

(9) Thielacker, W.; Knop, A.; Uffmann, H. *Angew. Chem.* **1965**, *77*, 717.

(10) Knight, G. T. *Chem. Commun.* **1970**, 1016.

(11) Layer, R. W. *Tetrahedron. Lett.* **1970**, 4413.

(12) Banks, R. E.; Haszeldine, R. N.; Miller, P. J. *Tetrahedron Lett.* **1970**, 4417.

(13) Filby, W. G.; Gunther, K. *Z. Naturforsch., Teil B*, **1977**, *32*, 693.

(14) Bowman, D. F.; Brokenshire, J. L.; Gillan, T.; Ingold, K. U. *J. Am. Chem. Soc.* **1971**, *93*, 6551.

(15) Wajer, Th. A. J. W.; Mackor, A.; De Boer, Th. J.; van Voorst, J. D. W. *Tetrahedron* **1967**, *23*, 4021.

(16) Russell, G. A.; Geels, E. J.; Smentowski, F. J.; Chang, K.-Y.; Reynolds, J.; Kaupp, G. *J. Am. Chem. Soc.* **1967**, *89*, 3821.

(17) Mulvey, D.; Waters, W. A. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1868.

(18) Mulvey, D.; Waters, W. A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1059.

(19) Waters, W. A. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1079.

(20) Camaggi, C. M.; Caser, M.; Placucci, G.; Guerra, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1675.

(21) Fairhurst, S. A.; Sutcliffe, L. H. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1521.

(22) Aurich, H. G.; Heinrich, J.-M.; Wassmuth, G. *J. Chem. Res. Suppl.* **1980**, 222, 224.

(23) Wajer, Th. A. J. W.; Mackor, A.; de Boer, Th. J. *Tetrahedron* **1969**, *25*, 175.

(24) There have also been many studies of the products formed when nitroso compounds react with organic substrates. The potential involvement of free radicals in most of these reactions was not specifically investigated. See, e.g., Shemyakin, M. M.; Maimind, V. I.; Vaichunaite, B. K. *Izv. Akad. Nauk, Otd. Khim. Nauk* **1957**, 1260. Banks, R. E.; Barlow, M. G.; Haszeldine, R. N. *J. Chem. Soc.* **1965**, 4714. Ginsburg, V. A.; Privezentseva, N. F. *Zh. Obshch. Khim.* **1968**, *38*, 832. Ginsburg, V. A.; Martynova, L. L.; Privezentseva, N. F.; Buchek, Z. A. *Ibid.* **1968**, *38*, 2505. Howe, R. K. *J. Org. Chem.* **1968**, *33*, 2848. Motherwell, W. B.; Roberts, J. S. *J. Chem. Soc., Chem. Commun.* **1972**, 329. Boyer, J. H. In "The Chemistry of the Nitro and Nitroso Groups", Feuer, H., Ed.; Interscience: New York, **1969**; Part 1, Chapter 5. Houben-Weyl "Methoden der Organischen Chemie"; Georg Thieme Verlag: Stuttgart, 1971; Band X, Teil 1, Chapters 3-5.

(25) Radicals can be formed from nitroso compounds by a nucleophilic attack on the nitroso group followed by oxidation of the resultant hydroxylamine anion by adventitious oxygen or an excess of the nitroso compound. See: Forrester, A. R.; Hepburn, S. P. *J. Chem. Soc. C* **1971**, 701.

0002-7863/81/1503-4833$01.25/0