

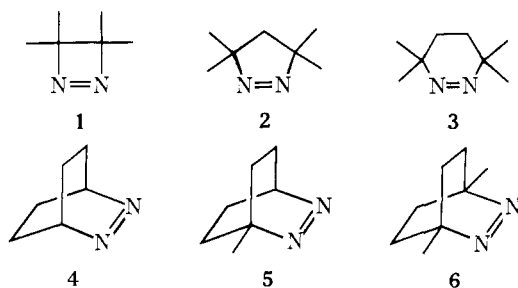
Extrusion of Nitrogen from Cyclic and Bicyclic Azo Compounds

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Abstract: A homologous series of three α,α' -tetramethyl monocyclic azoalkanes (1–3) has been decomposed thermally and photochemically. For the five- and six-membered compounds (2, 3), the sum of the ground state strain energy and ΔH^\ddagger of thermolysis is approximately equal to ΔH^\ddagger of decomposition of the model compound, azo-*tert*-butane (8). Diazetine (1), however, is at least 11 kcal mol⁻¹ more stable than its strain energy (24.5 kcal mol⁻¹) would predict. Fluorescence spectra have been obtained for 1 and 2, and quantum yields for loss of nitrogen from all three compounds have been measured: 1, 0.52; 2, 0.98; 3, 0.009. Thermolysis of three 2,3-diazabicyclo[2.2.2]octenes (4–6) has been studied with the aim of elucidating their decomposition mechanism. The surprisingly small effect of α -methyl groups as well as the high thermal stability of these azoalkanes is discussed in terms of ground and transition state energy.

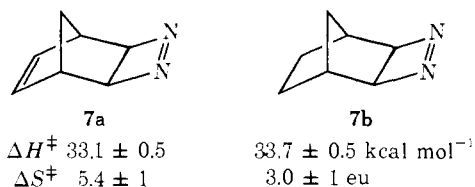
The thermal and photochemical lability of cyclic azo compounds depends strongly on their structure² but understanding the reasons for this dependence requires a knowledge of the ground and excited state energy surfaces. Approaches to the problem have relied on thermochemical,³ structural,⁴ and spectroscopic⁵ data in conjunction with theoretical calculations.⁶ We have studied a homologous series of three monocyclic azo compounds (1–3) and three bicyclic azo compounds



(4–6) which differ in bridgehead substitution. Thermolysis and photolysis were carried out on 1–3 in order to examine the effect of ring size on the facility with which nitrogen is lost. Thermolysis rates were measured for 4–6 in an effort to deduce the relative degree to which the C–N bonds are stretched in the transition state.

Results and Discussion

Thermal Decomposition of Monocyclic Azoalkanes. Rate constants and activation parameters for thermolytic extrusion of nitrogen from 1–3 are given in Table I, along with literature values. No previous kinetic data are available for 1, which was only recently synthesized,⁹ but two ring-fused diazetines (7a,b)



were found by Lemal and co-workers¹⁰ to have the activation parameters shown below. In view of the structural differences between 1 and 7a,b, we consider our activation parameters to be in reasonable agreement with the earlier ones. Pyrazoline 2 has been thermolyzed before in the gas phase⁷ and in ethylbenzene.^{8a} The gas-phase value does not differ from that obtained in solution by any more than the two solution values

differ from one another even though gas-phase determinations are generally fraught with more problems.¹¹ Although the values of ΔG^\ddagger found for 2 by the three groups of workers lie within 1 kcal mol⁻¹, ΔH^\ddagger differs by more than 2 kcal mol⁻¹. This discrepancy may be caused by a solvent effect, since it was recently discovered⁸ that many cyclic azo compounds decompose more slowly in polar solvents. The polarity¹² of diphenyl ether ($E_T = 35.3$) is slightly greater than that of ethylbenzene (toluene $E_T = 33.9$). Alternately, the variations may be merely another example of the inherent error in determination of activation parameters and of the known correlation of ΔH^\ddagger with ΔS^\ddagger due to such error.¹³ Since azo compounds are not usually subject to induced decomposition, the discrepancy is probably not the result of solvent radical scavenging ability.¹⁴ The activation parameters for the three separate determinations of 3 appear at first to be in good agreement; however, we find that the rates in hexadecane are definitely faster than those in diphenyl ether. This difference is not an artifact from two experimental methods of rate determination nor is it attributable to temperature discrepancies, as both were cross checked in our separate laboratories. It is most likely to be a real solvent effect, in accord with the results of Rüchardt.^{8a}

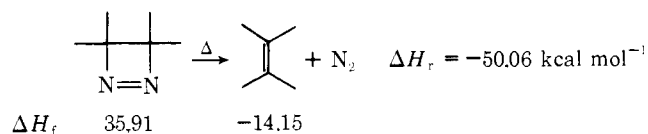
One of us suggested that for monocyclic azoalkanes, the sum of the ground state strain energy and ΔH^\ddagger for thermolysis was approximately constant.³ To examine the generality of this idea and to compare the result with other four-membered rings, we have determined the strain energy of diazetine 1. The heat of formation (ΔH_f) of crystalline 1 was found to be 21.0 \pm 0.3 kcal mol⁻¹¹⁵ from five bomb calorimetry experiments which consumed a heartbreaking total of 3.5 g of material. The heat of sublimation, as determined by Margret Mansson at the Thermochemical Laboratory of the University of Lund, Sweden,¹⁶ came out as 14.9 \pm 0.1 kcal mol⁻¹. From these two values, we calculate the strain energy of 1 to be 24.5 \pm 0.5 kcal mol⁻¹, based on *trans*-azo-*tert*-butane (8) as an unstrained model. Diazetines are therefore slightly less strained than other four-membered rings (cyclobutane, 26.2 kcal mol⁻¹; cyclobutene, 29.8; tetramethyldioxetane, 30.5).^{17,18a} Because the lowest ionization potential (IP) of 1 differs from that of 2 by only one-third of the IP difference between 2 and 3 (cf. Table IV) we suggest that repulsion between lone pairs, invoked³ to rationalize the higher ring strain of 3 relative to 2, is negligible in 1. Nonbonded methyl–methyl interactions would account for some of the strain in 1 but the energy involved is unlikely to exceed 2.5 kcal mol⁻¹, based on the effect of interfering *cis* methyl groups on the Cope rearrangement of divinylcyclobu-

Table II. Rate Constants and Activation Parameters for Bicyclo[2.2.2]azoalkanes

Compd	$k \times 10^4$, s^{-1}	Temp, °C	ΔH^\ddagger , $kcal\ mol^{-1}$	ΔS^\ddagger , eu	ΔG^\ddagger (513.15 K), $kcal\ mol^{-1}$	Ref
4	0.635	230.22	45.0 ± 0.2	10.6 ± 0.4	39.6	This work
	1.500	239.93				
	2.495	245.96				
	5.423	255.03				
	5.890	255.95				
5	0.819	224.91	43.5 ± 0.03	8.4 ± 0.1	39.2	32
	1.388	230.22				
	3.193	239.93				
	5.182	245.96				
	11.21	255.03				
6	1.271	220.02	43.7 ± 0.4	11.4 ± 0.9	37.9	This work
	2.019	224.91				
	3.382	230.22				
	7.595	239.93				
	12.50	245.96				

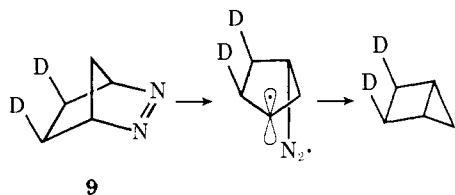
ochemistry of the decomposition of **1** may be of help and so might the effect of substituents on the rate of thermolysis. However, meaningful studies in these areas are likely to require advances in the synthesis of diazetines.

The production of electronically excited states by thermal reactions is an area of much current interest, particularly when the precursors are dioxetanes.^{18b} Thermodynamic considerations^{18a} show that the thermolysis of these fascinating compounds is sufficiently energetic to produce either singlet or triplet excited ketones. Applying the same reasoning to **1**, we calculate that thermolysis will be exothermic by about 50 kcal mol⁻¹, giving a total energy from transition state to products



of 50.1 + 31.7 = 81.8 kcal mol⁻¹. Thus, sufficient energy is available to produce a triplet²⁹ but not a singlet excited olefin.

The Effect of α -Methyl Groups on Thermolysis of Azoalkanes. It was noted previously³ that thermolysis of bicyclic azo compounds is more difficult than expected on the basis of their ring strain energy. In a bicyclo[2.2.2]azoalkane, the sum of the ring strain energy (10.1 kcal mol⁻¹) and ΔH^\ddagger for decomposition exceeded the usual 42 kcal mol⁻¹ transition state energy by nearly 12 kcal mol⁻¹. One of the tentative explanations set forth for this behavior was that nitrogen departs in a stepwise manner, conceivably a higher energy process than the usual concerted mechanism. This idea is precedented as the double inversion of stereochemistry observed in **9** led to the



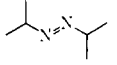
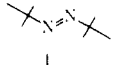
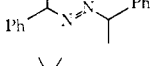
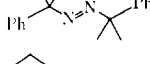



suggestion³⁰ that nitrogen is liberated by backside attack of the unpaired electron on the C-N bond of the diazenyl radical.

In order to test the stepwise mechanism experimentally, the Ramsperger criterion^{24,26,27} was applied to the thermolysis of **4-6**. According to this criterion, successive addition of radical stabilizing groups to the carbon α to the azo linkage should cause equal rate enhancement factors (n) if the mechanism is concerted two-bond cleavage. If, in the present compounds,

we assign a relative rate constant of 1.0 to **4**, the concerted mechanism predicts that k_{rel} for **5** and **6** should be n and n^2 , respectively. On the other hand, the stepwise mechanism predicts that k_{rel} for **5** and **6** should be n and $2n - 1$, respectively.³¹ Based on the effect of α -methyl groups on thermolysis rates of acyclic azoalkanes,²⁶ one would expect n to be nearly 15. The results of thermolysis studies on **4-6** are compiled in Table II, where it will be noted that all three compounds were run at the same temperature in several instances. In fact, the rate constants at 230.22, 239.93, and 245.96 °C are directly comparable because **4-6** were thermolyzed simultaneously in the same temperature-controlled bath. The results at 239.93 °C are typical; k_{rel} for **4-6** is 1.0, 2.13, and 5.06. Not only are the rate enhancements surprisingly small, but the second methyl group enhances the rate more than predicted by either mechanism. Nevertheless, the discrepancy between the observed k_{rel} for **6** (5.06) and that expected from concerted decomposition (4.53) is smaller than the discrepancy based on the stepwise mechanism (k_{rel} predicted 3.26). It seems most expedient to invoke the concerted mechanism and to attribute the ~10% discrepancy to experimental error or to a steric factor. However, we cannot rule out a mechanism analogous to that postulated for acyclic azoalkanes: the symmetry of the transition state reflects the stability difference of the incipient radicals.²⁶ The apparent contrast in the behavior of the [2.2.1] system **9** and the [2.2.2] system **4-6** remains an open question, though the stereochemical studies³⁰ which led to the suggestion of a stepwise mechanism for **9** are of a very different nature from the kinetic approach employed here. An alternative explanation³³ for the stereochemical outcome of the [2.2.1] system is a recoil force on carbons 1 and 4 exerted by the departing nitrogen; however, this idea has not been received enthusiastically.²² The situation with regard to vibrational energy in the biradical is even worse than was at first realized,²² for thermolysis of **9** to the cyclopentadiyl radical is endothermic by 10 kcal mol⁻¹.³⁴ A possible way to shed light on this matter would be to apply the Ramsperger criterion to the bicyclo[2.2.1] system.

An interesting question arises in considering the magnitude of the α -methyl effect. According to Table II, addition of two methyl groups to **4** causes a ΔG^\ddagger decrease of 1.7 kcal mol⁻¹. An effect of similar magnitude is seen in the pyrazolines (Table III), although more highly substituted pyrazolines behave strangely,⁷ giving actual rate retardation on further methylation. α -Methyl substitution in acyclic azoalkanes, however, lowers ΔG^\ddagger by 5 kcal mol⁻¹, as shown in Table III. Thus the effect of α -methyl groups in these cyclic and bicyclic systems is only one-third of that found in the acyclic series.

Table III. Activation Parameters for Selected Azo Compounds

Compd	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , eu	ΔG^\ddagger (513.15 K)	Ref
	46.7	14.1	39.4	35
	42.2	16.2	33.9	14
	32.1	7.6	28.2	36
	29.0	11.0	23.4	37
	41.4	11.4	35.6	7
	40.0	10.4	34.7	7
	39.3	10.3	34.0	7

At first sight, one is tempted to attribute this difference to an earlier transition state in the cyclic compounds. If the C-N bonds were less stretched in the transition state, a diminished effect of α substituents would certainly be expected. R uchardt and co-workers³⁸ have pointed out that acyclic cis azoalkanes have an earlier transition state than their trans counterparts, in accord with the higher energy of the cis isomers.²⁶ In the present case, thermolysis of the cyclic cis compounds is also less endothermic than that of trans but other evidence indicates that an earlier transition state is not a general explanation. Addition of α -vinyl or α -phenyl groups to pyrazolines facilitates decomposition by the same amount as do these structural changes in acyclic compounds.⁴⁰ Similarly, the α -deuterium isotope effects in 1-pyrazolines are comparable to those in acyclic systems.⁴² It therefore appears that in 1-pyrazolines and presumably also the series 4-6, only alkyl groups are poor accelerators of the decomposition rate.

This observation can be rationalized in terms of either transition state or ground state effects. In the transition state for bicyclic azoalkane thermolysis, the developing radical is forced to reside in an sp³-like orbital rather than a p orbital, owing to bond angle compression by the ring, e.g., **11**. Overlap

**11**

of the C-H bonds of the α -alkyl groups with the radical center (hyperconjugation) is less favorable under these circumstances, as evidenced by the small β hyperfine coupling constants in pyramidal (sp³) radicals.⁴³ It follows that alkyl groups should not stabilize the cyclic transition state as much as they do in acyclic compounds, where hyperconjugation is unrestricted.⁴⁴ The fact⁴⁵ that methyl substitution favors pyramidal radical geometry has been neglected because the barrier to inversion in the *tert*-butyl radical is small compared to the enhancement of radical stability by additional alkyl groups. To complete this explanation, one must postulate that conjugating groups are relatively insensitive to radical geometry, a proposal which admittedly lacks verification. The influence of radical geometry on hyperconjugation might be ascertained by examining α -methyl effects in larger bicyclic systems, but not in six-membered azoalkanes where tautomerization is a serious problem.⁴⁶ An alternate rationalization of the small rate enhancement is that methyl groups stabilize the ground state of

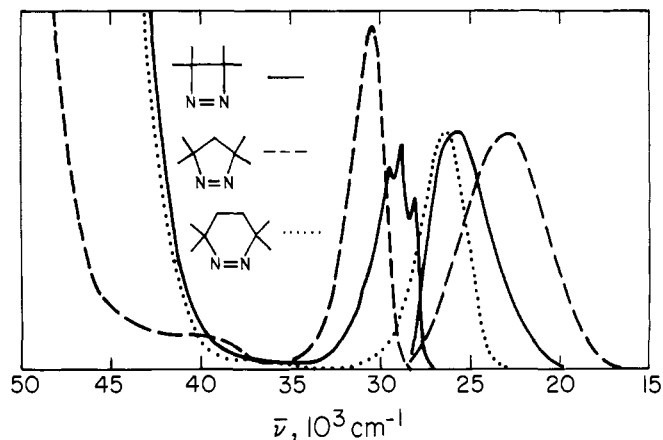


Figure 2. Absorption and fluorescence spectra of cyclic azoalkanes. Fluorescence curves lie to the right of the absorption spectrum for each of the two compounds which emit. Fluorescence intensities are arbitrary but absorption intensities are proportional to extinction coefficients. For further details, see Table IV.

cyclic azoalkanes nearly as much as they do the transition state. This explanation has been set forth for isomerization of bicyclo[2.2.0]hexanes, where bridgehead alkyl substitution is said to reduce the ground state ring strain energy, resulting in an actual increase of the activation energy for opening of the central bond to a diradical.⁴⁷ Although pyrazolines and bicyclo[2.2.2]azoalkanes are far less strained than bicyclo[2.2.0]hexanes, it is still possible that these azo compounds are stabilized by alkyl groups more than acyclic azoalkanes are.⁴⁸ This explanation is subject to experimental scrutiny by thermochemical techniques.

The picture of the transition state for thermolysis of **6** which evolves from the above discussion has bond angles similar to those of starting material. Since virtually all of the ring strain would be retained in such a structure, it is not surprising that the thermolysis of 4-6 proceeds with much more difficulty than its ground state strain would predict. Although this idea is sufficient to explain the facts, one cannot rule out the suggestion offered for **1** (vide supra) that nitrogen extrusion requires some motion which is restricted by rigid structures.

Photolysis of Monocyclic Azoalkanes. Irradiation of azo compounds generally leads to loss of nitrogen,⁴⁹ although the efficiency of this process varies widely.⁵⁰ In an attempt to understand these variations, we determined nitrogen quantum yields and fluorescence quantum yields for 1-3 (cf. Table IV). The absorption and fluorescence spectra obtained in this work are shown in Figure 2.

Looking first at the absorption spectra, we note that the λ_{\max} of **2** is at shorter wavelength than that of **3**, exactly the trend predicted⁵³ by the smaller bond angles in **2**. The longest wavelength band in azoalkanes is an $n-\pi^*$ transition, whose energy should be raised as the n -combination of nonbonding orbitals is lowered by decreasing the bond angles. As expected, the smaller C-N=N bond angle in the five-membered ring (**2**)⁵⁴ raises its lowest ionization potential(IP) above that of **3**. The IP of **1** is 0.24 eV higher than that of **2**, again the trend expected on the basis of bond angles. However, the high IP of **1** predicts that its absorption maximum ought to be at a shorter wavelength than that of **2**, in sharp disagreement with experiment (cf. Figure 2 and Table IV). Clearly, the assumed constancy of the π^* orbital energy in the proposed correlation⁵³ of λ_{\max} with bond angle no longer holds in **1**. Despite the utility of this correlation in acyclic azoalkanes,³⁹ caution will be required in applying it to cyclic systems.

Fluorescence has been observed previously in several cyclic azoalkanes⁵⁵ but no comprehensive study of this phenomenon

recrystallization from 2-methylbutane, and sublimation. Its physical and spectral data were identical with those reported.⁹

***N*-Toluenesulfonyl-3,5,5-trimethyl-2-pyrazoline.** To 1000 mL of dry dichloromethane in a 3000-mL three-neck flask were added 112 g (1 mol) of 3,5,5-trimethyl-1-pyrazoline⁶⁵ (prepared from hydrazine and mesityl oxide) and 123 g (1.22 mol) of triethylamine. The stirred mixture was cooled to -15°C under nitrogen and 210 g (1.10 mol) of toluenesulfonyl chloride was added. A smooth reaction ensued, as evidenced by the gradual formation of solid. After 1 hr at -15°C , the mixture was allowed to warm to ambient temperature, after which it was refluxed for 30 min. Addition of water gave a two-phase, light brown, clear solution. The organic layer was removed and the aqueous layer extracted with dichloromethane. The combined organic phases were washed in succession with 2 N HCl, aqueous NaHCO_3 , and saturated NaCl. After drying over MgSO_4 , the dark solution was filtered. To the boiling dichloromethane solution was added an equal volume of hexane and the mixture was allowed to stand overnight in the refrigerator. The light yellow product was filtered off and a second crop recovered by concentration of the filtrate. After recrystallization from ethyl acetate the product was obtained in 61% yield; mp $162\text{--}166^{\circ}\text{C}$ dec; NMR (CDCl_3) δ 1.50 (s, 6 H), 1.93 (t, $J = 1$ Hz, 3 H), 2.40 (s, 3 H), 2.60 (q, $J = 1$ Hz, 2 H), 7.25 (d, $J = 8$ Hz, 2 H), 7.86 (d, $J = 8$ Hz, 2 H).

Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{SO}_2$: C, 58.62; H, 6.81. Found: C, 58.89; H, 6.77.

3,3,5,5-Tetramethyl-1-pyrazoline (2). A solution of 53.2 g (0.2 mol) of *N*-toluenesulfonyl-3,5,5-trimethyl-2-pyrazoline in 1000 mL of dry THF was prepared by mild heating in a 2000-mL three-neck flask fitted with a thermometer, mechanical stirrer, and constant rate addition funnel. After the solution was cooled to -50°C , 245 mL of 0.82 M methylolithium (0.2 mol) in ether was added over a 2-h period. The mixture was allowed to warm to ambient temperature and water was added to dissolve the suspended brown solid. The water layer was extracted with ether and all combined ether extracts were washed with saturated NaCl and dried with K_2CO_3 . Distillation of the ether and THF at atmospheric pressure followed by vacuum distillation of the residue gave the desired product in 22% yield, bp 59°C (29 mm) (lit.^{8a} 72°C (11 mm)). Further purification was effected by twice recrystallizing from pentane at -78°C under nitrogen, followed by a second vacuum distillation. No impurities could be detected by GC on a 4 ft \times 0.25 in. column of QF-1 at 92°C : UV (hexane) 327 nm (ϵ 204) [lit. (hexane) 327 (190),⁵⁶ (ethylbenzene) 325–330 (165),^{8a} (methanol) 324 (160)⁶⁶].

3,3,6,6-Tetramethyl-1,2-diazacyclohex-1-ene was made by the IF_5 oxidation of commercially available 2,5-diamino-2,5-dimethylhexane,⁶⁷ or better, by the sodium tungstate/hydrogen peroxide procedure:⁹ bp 62°C (12 mm) (lit. bp $48\text{--}50^{\circ}\text{C}$ (4.2 mm),⁹ 48°C (4 mm));⁶⁷ UV (hexane) 380 nm (ϵ 138) (lit. (ethylbenzene) 380 (154)).^{8a}

Anal. Calcd for $\text{C}_8\text{H}_{16}\text{N}_2$: C, 68.52; H, 11.50. Found: C, 68.75; H, 11.60.

2,3-Diazabicyclo[2.2.2]octenes. The bicyclic azoalkanes **4–6** were prepared by the cycloaddition of *N*-methyl-1,2,4-triazoline-3,5-dione⁶⁸ to the appropriate diene. Since **4** and **6** are known compounds,^{32,69} only the detailed procedure for **5** will be given. In this work, **4** and **6** were also made by the triazolinedione method, which is superior to using diethyl azodicarboxylate.^{32,69}

1,4-Dimethyl-2,4,6-triaza[5.2.2.0^{2,6}]tricycloundec-8-ene-3,5-dione. 1-Methylcyclohexa-1,4-diene was prepared by the Birch reduction of toluene, following the procedure for *o*-xylene.⁷⁰ The distilled diene was isomerized by adding 110 g of it at 25°C to a solution of 16.4 g of anhydrous potassium *tert*-butoxide in 1200 mL of Me_2SO , which had been dried by distillation from CaH_2 . The mixture was stirred and heated to 100°C under N_2 , while aliquots were worked up according to Schriesheim⁷¹ and analyzed by GC (250-ft capillary column of SF-96 at 70°C). The relative retention times follow: ethyl acetate, 1.00; toluene, 1.68; 1-methylcyclohexa-1,3-diene, 1.71; a major impurity (probably 2-methylcyclohexa-1,3-diene), 1.82; 1-methylcyclohexa-1,4-diene, 2.00. After 1.5 h, the diene mixture had reached equilibrium ($\sim 40\%$ 1-methylcyclohexa-1,3-diene) so the dark yellow solution was cooled in an ice bath and diluted with 1000 mL of water. The mixture was then extracted with four 250-mL portions of pentane and the combined extracts were dried over K_2CO_3 . Distillation at 1 atm afforded 75 g of a diene mixture boiling at $102\text{--}107^{\circ}\text{C}$.

A 12.7-g (0.11 mol) portion of powdered 4-methylurazole⁶⁸ was suspended in 200 mL of ethyl acetate under N_2 . To the mixture was

added portionwise 11.9 g (0.11 mol) of *tert*-butyl hypochlorite while maintaining the temperature below 20°C . After addition was complete, the bright red, homogeneous solution was stirred for 30 min and the solvent was then removed by rotary evaporation at 25°C . The dry residue was redissolved in ethyl acetate and filtered to remove suspended solid, and the filtrate was added dropwise to an ice-cold, well-stirred solution of 20 g of 40% pure 1-methylcyclohexa-1,3-diene in 250 mL of ethyl acetate. The progress of the reaction was monitored by GC on the SF-96 capillary column. Addition of dienophile was stopped when the 1-methylcyclohexa-1,3-diene was about 90% gone but before any of the peak attributed to the 2-methyl isomer had reacted. The cloudy, white mixture was rotary evaporated to dryness and the solid was freed of residual dienes by evacuation with a mechanical pump. Several recrystallizations from ethyl acetate/hexane afforded white Diels–Alder adduct: mp $107\text{--}111^{\circ}\text{C}$; NMR (CDCl_3) δ 1.2–2.6 (br m), 1.92 (s, 3 H), 3.00 (s, 3 H), 4.90 (br s, 1 H), 6.45 (m, 2 H).

Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_2$: C, 57.96; H, 6.32. Found: C, 58.17; H, 6.31.

1-Methyl-2,3-diazabicyclo[2.2.2]oct-2-ene. A solution of the above Diels–Alder adduct (5 g) in 200 mL of absolute ethanol was hydrogenated with 50 mg of 10% Pd/C catalyst on a Parr hydrogenator at 40 psi. The reaction was complete in 1.5 h, after which the catalyst was filtered off and the filtrate rotary evaporated to dryness. The crude product, a viscous oil, showed characteristic NMR peaks (CCl_4) at δ 1.60 (s, 3 H), 1.87 (br s), 2.96 (s, 3 H), 4.24 (br s, 1 H). Cleavage of the urazole moiety was effected with sodium methoxide in Me_2SO .

Sodium metal (2.5 g) was allowed to dissolve in 100 mL of methanol under N_2 . The excess methanol was removed by evacuation with a mechanical pump and the residue was finally heated for 30 min at 80°C under vacuum. After cooling, the sodium methoxide thus prepared was dissolved in 50 mL of Me_2SO which had been dried by distillation from CaH_2 . To this solution was added 3.5 g of the hydrogenated adduct prepared above, dissolved in 30 mL of Me_2SO , and the resulting mixture was heated under N_2 at 80°C for 12 h. The tan solution was cooled and poured slowly into 400 mL of ice water, after which sufficient 6 N HCl was added to bring the pH to 7. Aqueous 2 M CuCl_2 was added dropwise with stirring, causing formation of a red-brown precipitate and a decrease of the pH. Periodic addition of ammonium hydroxide was necessary to keep the pH at 7.⁷² When the precipitate ceased to form, it was filtered off and washed with 20% aqueous NH_4Cl , 95% ethanol, and cold water.

The resulting cuprous chloride complex was decomposed by adding it to 1 g of NaOH in 40 mL of H_2O and continuously extracting with pentane. The pentane was distilled off and the oily residue was distilled: bp 121°C (40 mm); NMR (CDCl_3) δ 0.8–1.9 (br m), 1.75 (s, 3 H), 5.20 (br s, 1 H); UV (hexadecane) 380 nm (ϵ 200). The purity of **5** was checked by GC on a 10 ft \times 0.25 in. column of 10% XE-60 on Chromosorb W at 135°C and on a 6 ft \times 0.125 in. column of 10% XF-1150 on Chromosorb W AW DMCS at 100°C . When the Diels–Alder reaction with mixed methylcyclohexa-1,3-dienes was carried out without cooling, a new peak appeared in the GC traces of the resulting azo compound **5**. In one case, this peak was 10% of the total area and the NMR spectrum of this sample revealed a new doublet ($J = 6$ Hz) at δ 0.8 ppm. Since this chemical shift agrees with that reported for the methyl group of 5-*endo*-methyl-2,3-diazabicyclo[2.2.1]heptene-2,³⁰ we assign the impurity to 5-*endo*-methyl-2,3-diazabicyclo[2.2.2]octene-2, derived from Diels–Alder reaction of the wrong diene in the mixture (2-methylcyclohexa-1,3-diene). Since the presence of isomeric impurities is not revealed by elemental analysis of either the Diels–Alder adduct or the final product **5**, and since this particular isomer would vitiate the kinetic results, we were especially careful to ensure its absence in the samples of **5** used in the kinetic studies.

Kinetics. Nitrogen evolution kinetics were carried out on the previously described constant volume apparatus.⁷³ The UV kinetics were carried out by preparing approximately 0.006 M solutions of the azo compounds in hexadecane (Aldrich, 99%) and syringing 3-mL aliquots into Pyrex cuvettes. The samples were degassed by two freeze–thaw cycles and sealed under vacuum, and a UV spectrum was run on each cuvette. Five cuvettes for each compound at each temperature were preheated to 100°C and plunged into a regulated silicone oil bath (Bayley temperature controller). Temperature was measured using a Minco calibrated platinum resistance thermometer. After removal at the appropriate interval (up to 3 half-lives) the absorbance was

noted and the tubes were returned to the bath for 10 half-lives. A conventional first-order treatment gave the rate constants at each temperature and a least-squares fit of $\ln(k/T)$ vs. $1/T$ gave ΔH^\ddagger and ΔS^\ddagger .

Photochemistry. Fluorescence quantum yields were determined by comparing the corrected integrated emission bands of the azoalkanes with that of phenanthrene using an excitation wavelength of 335 nm for all compounds. The fluorescence quantum yield of phenanthrene in aerated spectroquality hexane was taken as 0.031.⁷⁴ Photolyses were conducted on a conventional merry-go-round, using appropriate solution filters for wavelength isolation.⁷⁵ Nitrogen evolution was measured by means of a Toepler pump and gas buret.

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References and Notes

- (1) (a) Rice University; (b) University of New Orleans.
- (2) For a review, see K. Mackenzie in "The Chemistry of the Hydrato, Azo, and Azoxy Groups", Vol. 1, S. Patai, Ed., Wiley, New York, N.Y., 1975, p 329.
- (3) P. S. Engel, *J. Am. Chem. Soc.*, **98**, 1972 (1976), and references cited therein.
- (4) T. Otterson, C. Rømming, and J. P. Snyder, *Acta Chem. Scand., Ser. B*, **30**, 407 (1976); R. D. Suenram, *J. Mol. Spectrosc.*, **33**, 1 (1976).
- (5) R. J. Boyd, J. C. G. Bunzli, and J. P. Snyder, *J. Am. Chem. Soc.*, **98**, 2398 (1976); K. N. Houk, Y. M. Chang, and P. S. Engel, *ibid.*, **97**, 1824 (1975).
- (6) See, for example, R. N. Camp, I. R. Epstein, and C. Steel, *J. Am. Chem. Soc.*, **99**, 2453 (1977).
- (7) R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3963 (1966).
- (8) (a) W. Duismann and C. Rüchardt, *Chem. Ber.*, in press; *Tetrahedron Lett.* 3883 (1976); (b) H. Olsen and J. P. Snyder, *J. Am. Chem. Soc.*, **100**, 285 (1978).
- (9) F. D. Greene and K. E. Gilbert, *J. Org. Chem.*, **40**, 1409 (1975).
- (10) N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *J. Am. Chem. Soc.*, **91**, 5668 (1969).
- (11) (a) A. U. Blackham and N. L. Eatough, *J. Am. Chem. Soc.*, **84**, 2922 (1962); (b) C. Steel and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 975 (1959); (c) D. F. McMillen, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **94**, 4403 (1972).
- (12) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).
- (13) R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961). A plot of ΔH^\ddagger vs. ΔS^\ddagger for **2** is linear, using values from Table I.
- (14) J. C. Martin and J. W. Timberlake, *J. Am. Chem. Soc.*, **92**, 978 (1970).
- (15) All tolerances expressed in this paper are the standard deviation.
- (16) Details of these experiments will be reported elsewhere: R. L. Montgomery, M. Mansson, P. S. Engel, R. A. Leckonby, S. Szilagy, J. W. Timberlake, and F. D. Rossini, *J. Chem. Eng. Data*, in press.
- (17) S. W. Benson and H. E. O'Neal, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., No. 21*, 271 (1970).
- (18) (a) G. Hohne, A. H. Schmidt, and P. Lechtken, *Tetrahedron Lett.*, 3587 (1976); (b) N. J. Turro, P. Lechtken, N. E. Schore, G. Schuster, H. C. Steimetzler, and A. Yekta, *Acc. Chem. Res.*, **7**, 97 (1974).
- (19) J. A. Berson, P. B. Dervan, R. Malherbe, and J. A. Jenkins, *J. Am. Chem. Soc.*, **98**, 5937 (1976).
- (20) R. A. R. Pearce, I. W. Levin, and W. C. Harris, *J. Chem. Phys.*, **59**, 1209, 3048 (1973).
- (21) The authors thank Dr. Ira W. Levin for helpful discussion of this point.
- (22) R. G. Bergman in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973.
- (23) P. Dowd and M. Chow, *J. Am. Chem. Soc.*, **99**, 6438 (1977).
- (24) R. J. Crawford and M. Ohno, *Can. J. Chem.*, **52**, 3134 (1974).
- (25) ΔG^\ddagger for decomposition of 3,6-dicyano-3,6-dimethyl-1,2-diazacyclohex-1-ene²⁶ is lower than that for **3** by even more than ΔG^\ddagger for azoisobutyronitrile is lower than that for **8**. Since symmetrical acyclic azoalkanes decompose by two-bond scission,^{26,27} it is likely that the six-membered compounds proceed by the same mechanism.
- (26) P. S. Engel and D. J. Bishop, *J. Am. Chem. Soc.*, **97**, 6754 (1975).
- (27) J. Hintz, A. Oberlinner, and C. Rüchardt, *Tetrahedron Lett.*, 1975 (1973); H. C. Ramsperger, *J. Am. Chem. Soc.*, **51**, 2134 (1929).
- (28) As an example of non-least-motion cleavage, twisting about the N=N bond is apparently required for dissociation of azo dioxides. See R. Hoffmann, R. Gleiter, and F. B. Mallory, *J. Am. Chem. Soc.*, **92**, 1460 (1970).
- (29) The triplet energy of 2-butene is 80 kcal mol⁻¹: R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *J. Am. Chem. Soc.*, **95**, 2549 (1973).
- (30) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, **702**, 1 (1967).
- (31) The term $2n - 1$ is derived by assuming that k_{rel} for **5** is the average of the values for **4** and **6**.
- (32) S. G. Cohen and R. Zand, *J. Am. Chem. Soc.*, **84**, 586 (1962).
- (33) E. L. Allred and R. L. Smith, *J. Am. Chem. Soc.*, **89**, 7133 (1967).
- (34) This estimate is based on the experimental ΔH_f of **9**³ and the calculated ΔH_f of the cyclopentadiyl diradical from data in ref 17.
- (35) M. J. Perona, P. C. Beadle, and D. M. Golden, *Int. J. Chem. Kinet.*, **5**, 495 (1973).
- (36) S. G. Cohen, S. J. Groszos, and D. R. Sparrow, *J. Am. Chem. Soc.*, **72**, 3947 (1950).
- (37) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 137 (1966).
- (38) A. Schulz, N. T. Giac, and C. Rüchardt, *Tetrahedron Lett.*, 845 (1977). These workers found that *cis*-azo-1-methylcyclohexane decomposes about 100 times faster than *cis*-azo-1-methylcyclopentane, whereas the *trans* cyclohexyl compound is about one-third as fast as the *trans* cyclopentyl homologue. Part of the reason for the high stability of *cis*-azo-1-methylcyclopentane could be a smaller effective size of the alkyl moiety, as evidenced by its blue-shifted visible absorption maximum³⁵ relative to that of *cis*-azo-1-methylcyclohexane.
- (39) P. S. Engel, R. A. Melaugh, M. A. Page, S. Szilagy, and J. W. Timberlake, *J. Am. Chem. Soc.*, **98**, 1971 (1976).
- (40) $\Delta\Delta G^\ddagger$ (513.15 K) values are as follows: *trans*-3,5-dimethyl-1-pyrazoline⁷ minus *trans*-3,5-divinyl-1-pyrazoline²⁴ = 10.4 kcal mol⁻¹, azoethane³⁵ minus 3,3'-azo-1-propene³⁶ = 11.1 kcal mol⁻¹, azo-*tert*-butane¹⁴ minus 3,3'-azo-3-methyl-1-butene²⁶ = 10.4 kcal mol⁻¹, *trans*-3,5-dimethyl-1-pyrazoline⁷ (10, Table III) minus *trans*-3,5-diphenyl-1-pyrazoline⁴¹ = 8.7 kcal mol⁻¹, azoisopropane^{26,35} minus azo- α -phenylethane^{26,36} = 11.0 kcal mol⁻¹, azo-*tert*-butane minus azocumene³⁷ = 11.1 kcal mol⁻¹.
- (41) B. K. Bandlish, A. W. Garner, M. L. Hodges, and J. W. Timberlake, *J. Am. Chem. Soc.*, **97**, 5856 (1975).
- (42) B. H. Al-Sader and R. J. Crawford, *Can. J. Chem.*, **48**, 2745 (1970).
- (43) P. J. Krusic, T. A. Rettig, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 995 (1972); T. Kawamura, M. Matsunaga, and T. Yonezawa, *J. Am. Chem. Soc.*, **100**, 92 (1978).
- (44) A calculation using STO-3G shows that methyl substitution stabilizes planar radicals slightly more than it does pyramidal ones. We thank L. Domelsmith and K. N. Houk (Louisiana State University) for this calculation. Others have argued cogently that hyperconjugation is of minor importance in determining free radical stability. See C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).
- (45) P. J. Krusic and P. Meakin, *J. Am. Chem. Soc.*, **98**, 228 (1976); P. J. Krusic and R. C. Bingham, *ibid.*, **98**, 230 (1976).
- (46) P. B. Dervan and T. Uyehara, *J. Am. Chem. Soc.*, **98**, 1262 (1976).
- (47) R. K. Solly and E. N. Cain, *Int. J. Chem. Kinet.*, **8**, 563 (1976).
- (48) The ring strain of adamantane is decreased by added methyl groups. See W. V. Steele and I. Watt, *J. Chem. Thermodyn.*, **9**, 843 (1977), and references cited therein.
- (49) P. S. Engel and C. Steel, *Acc. Chem. Res.*, **6**, 275 (1973).
- (50) H. Durr and B. Ruge, *Top. Curr. Chem.*, **66**, 53 (1976).
- (51) L. N. Domelsmith, K. N. Houk, J. W. Timberlake, and S. Szilagy, *Chem. Phys. Lett.*, **48**, 471 (1977); K. E. Gilbert, *J. Org. Chem.*, **42**, 609 (1977).
- (52) C. J. Nalepa, unpublished results at Rice University.
- (53) N. C. Baird, P. de Mayo, J. R. Swenson, and M. C. Usselman, *J. Chem. Soc., Chem. Commun.*, 314 (1973).
- (54) For comparison, the C=C=C bond angle in cyclopentene is calculated to be 111.8° while that angle in cyclohexene is 123.50°. See O. Ermer and S. Lifson, *J. Am. Chem. Soc.*, **95**, 4121 (1973); K. F. Chiang and S. H. Bauer, *ibid.*, **91**, 1898 (1969).
- (55) S. D. Andrews and A. C. Day, *Chem. Commun.*, 477 (1967); A. C. Day and T. R. Wright, *Tetrahedron Lett.*, 1067 (1969); C. Steel and T. F. Thomas, *Chem. Commun.*, 900 (1966); G. L. Loper and F. H. Dorner, *J. Am. Chem. Soc.*, **95**, 20 (1973).
- (56) M. J. Mirbach, K. C. Kiu, M. F. Mirbach, W. R. Cherry, N. J. Turro, and P. S. Engel, *J. Am. Chem. Soc.*, in press.
- (57) Low-temperature fluorescence was attempted using a phosphorescence attachment on a Hitachi MPF-2A fluorescence spectrometer, without the rotating can. Since scattered light is a severe problem in this crude setup, we certainly do not rule out the possibility of emission from **3**. Better results were obtained with **1**, whose fluorescence became structured at -196 °C with a 0-0' band at 374 nm.
- (58) P. S. Engel and L. Shen, *Can. J. Chem.*, **52**, 4040 (1974).
- (59) D. E. Applequist, M. A. Lintner, and R. Searle, *J. Org. Chem.*, **33**, 254 (1968). The solvent in this experiment was probably the principal light absorber.
- (60) W. D. K. Clark and C. Steel, *J. Am. Chem. Soc.*, **93**, 6347 (1971).
- (61) M. Gisin and J. Wirz, *Helv. Chim. Acta*, **59**, 2273 (1976).
- (62) (a) C. G. Overberger, M. S. Chi, and D. G. Pucci, *Tetrahedron Lett.*, 4565 (1972); (b) G. Vitt, E. Hadicke and G. Quinkert, *Chem. Ber.*, **109**, 518 (1976).
- (63) R. Bonneau, J. Jousot-Dubien, L. Salem, and A. Y. Yarwood, *J. Am. Chem. Soc.*, **98**, 4329 (1976).
- (64) O. L. Chapman and R. A. Hayes, University of California, Los Angeles.
- (65) N. Kizhner, *J. Russ. Phys. Chem. Soc.*, **44**, 165 (1911); *Chem. Abstr.*, **6**, 1431 (1912).
- (66) R. J. Crawford, A. Mishra, and R. J. Dummel, *J. Am. Chem. Soc.*, **88**, 3959 (1966).
- (67) N. A. Porter, Ph.D. Thesis, Harvard University, 1969.
- (68) R. C. Cookson, S. S. Gupte, I. D. R. Stevens, and C. T. Watts, *Org. Synth.*, **51**, 121 (1972).
- (69) P. S. Engel, *J. Am. Chem. Soc.*, **91**, 6903 (1969).
- (70) L. A. Paquette and J. H. Barrett, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 467.
- (71) A. Schriesheim, R. J. Muller, and C. A. Rowe, *J. Am. Chem. Soc.*, **84**, 3164 (1962).
- (72) See procedure for preparation of 2,3-diazabicyclo[2.2.1]hept-2-ene by P. G. Gassman and K. T. Mansfield, ref 70, p 96.
- (73) J. W. Timberlake and J. C. Martin, *Rev. Sci. Instrum.*, **44**, 151 (1973).
- (74) Calculated from the fluorescence quantum yield and lifetime of phenanthrene in degassed solution. I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed, Academic Press, New York, N.Y., 1971, pp 28, 376.
- (75) The spectral output of the lamp and filter was examined by a monochromator and photomultiplier.