should be attributed to flexibility around the Cys residue.

The NH and C=O stretching regions of the IR spectra of peptides can be utilized to infer the state of hydrogen bonding at these functionalities. Bystrov et al. studied a terminally blocked dipeptide, Z-Ala-Ala-OMe, in dilute CCl<sub>4</sub> solution.<sup>21</sup> Out of two NH stretchings (3420 and 3340 cm<sup>-1</sup>), the low-frequency band was assigned to the intra- or intermolecular hydrogen-bonded NH group. In the present case, the IR spectrum of Z-Cys-Gly-Ala-OMe shows NH bands at 3405 and 3325 cm<sup>-1</sup> and CO bands at 1678 cm<sup>-1</sup> at room temperature (Figure 5b). At 233 K, new bands appear at 3280 and 1661 cm<sup>-1</sup>. These are thought to be due to intermolecular association through NH--O=C type hydrogen bonding.

The IR spectrum of  $[Fe_4S_4(Z-Cys-Gly-Ala-OMe)_4]^{2-}$  exhibits NH and C=O stretchings at 3300 and 1660 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub> at 298 K. On cooling at 243 K no new band appears (see Figure 5a). Thus, the above-mentioned intermolecular association does not take place. Then, two types of intramolecular hydrogen bonding are possible. The NH---O=C hydrogen bonding responsible for the  $\beta_{II}$  turn of the peptide is improbable due to steric reasons for this particular tripeptide. The NH---S type intramolecular hydrogen bonding is sterically best prefered and promoted by the anionic character of the thiolate group (see Figure 6). The IR data (Figure 5c) for  $[Fe_4S_4(Z-cys-Gly-OMe)_4]^{2-}$ indicate the absence of intermolecular association. The coordinated peptide is too short to make the hydrogen bond to thiolate sulfur but is just right for forming an NH hydrogen bond to bridging inorganic sulfide.

Sweeny and Magliozzo have explained the positive shift of native ferredoxins on the basis of their deuteration study on oxidized *C. pasteurianum* ferredoxin, that is NH---S bonds are not important in modifying the redox potential of the  $Fe_4S_4^{2+}$  cluster, contributing at best  $-0.2 \pm 0.8$  mV.<sup>9</sup> However, our results suggested that formation of the NH---S bonds stabilized in CH<sub>2</sub>Cl<sub>2</sub> at low temperature contributes to the shift of the redox potentials (120 mV at 233 K) to the positive side. Two interpretations are possible: (1) charge on the thiolato ligand is delocalized though the NH---S bond or (2) conformational folding around the thiolato ligand brings about distortion of the  $Fe_4S_4$  core.

Our observation of a slightly negative shift of the redox potential for  $[Fe_4S_4(SCH_2Ph)_4]^{2-}$  in  $CH_2Cl_2$  at low temperature indicates that the freezing of conformational rotation around the phenyl groups at low temperature probably contributes to a slight change of the redox potential. Actually, in the <sup>1</sup>H NMR spectra of  $[Fe_4S_4(SCH_2Ph)_4]^{2-,3-,23}$  the 2- complex exhibits an upfield shift of methylene protons, but those of the 3- complex show a downfield shift with a decrease in temperature. Such an effect of phenyl groups on the redox potentials of various types of ferredoxins has been noted.<sup>24</sup> More detailed investigations are required for further discussion on the effect of the phenyl groups in a solvent with a low dielectric constant, associated with interpretation of the role of Phe or Tyr residue located in the vicinity of the Fe<sub>4</sub>S<sub>4</sub> core.

### Summary

A positive shift in redox potential of  $[Fe_4S_4(Z-cys-Gly-Ala-OMe)_4]^{2-}$  was observed in CH<sub>2</sub>Cl<sub>2</sub> at 233 K. No shift was detected in the case of  $[Fe_4S_4(Z-cys-Gly-Ala-OMe)_4]^{2-}$  in DMF or  $[Fe_4S_4(Z-cys-Gly-OMe)_4]^{2-}$  in CH<sub>2</sub>Cl<sub>2</sub> even at low temperature. Our observation strongly suggests that the positive shift of the redox potential is attributed to the NH---S bond between Ala NH and Cys S in the Z-Cys-Gly-Ala-OMe part of the complex. Also, our finding suggests that chemical function of the peptide chain around sites in iron-sulfur proteins could be realized by a special conformation which induces hydrophobic environments.

**Registry No. 1**, 87532-20-5; **2**, 87532-22-7;  $[Fe_4S_4(S-t-Bu)_4][NMe_4]_2$ , 52678-92-9; Z-Cys-Gly-OMe, 85134-27-6; Z-Cys-Gly-Ala-OMe, 87532-23-8; Z-Cys(ACM)-Gly-OMe, 78658-27-2; Z-Cys(ACM)-Gly-Ala-OMe, 87532-24-9; CH<sub>2</sub>Cl<sub>2</sub>, 75-09-2.

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# Thermolysis of Azoalkanes Containing the 2,3-Diazabicyclo[2.2.2]oct-2-ene (DBO) Skeleton

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Abstract: The effect of one and two bridgehead substituents on the thermal stability of DBO is assessed by monitoring the disappearance of four new compounds (8-11). Two cyclopropyl groups are found to lower  $\Delta G^*$  for thermolysis by twice the amount of one such group; however, a second bridgehead phenyl substituent is much less effective than the first. Comparison of these results with those of the previously studied methyl and vinyl DBO suggests two mechanisms that are indistinguishable on the basis of available data. In the first one, symmetrical azoalkanes decompose by simultaneous scission of both C-N bonds while unsymmetrical azoalkanes exhibit greater breaking of the weaker C-N bond at the transition state. This idea is described in a More O'Ferrall-Jencks-Thornton diagram. The second possible mechanism is reversible cleavage of the weaker C-N bond followed by loss of nitrogen from an intermediate diazenyl radical. Incorporation of endocyclic fused rings into the DBO skeleton generally slows down thermolysis, perhaps by inhibiting planarization of the carbon atoms  $\alpha$  to the azo group.

The thermal stability of azoalkanes depends strongly upon their structure.<sup>1-3</sup> Among the most stable azoalkanes, one finds 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO), which was studied over two decades ago by Cohen and Zand.<sup>4</sup> Since that time, thermolysis

of several other DBO derivatives (e.g., 1-7) has been reported. Bridgehead methyl groups were found to exert such a small effect on thermal stability that it was difficult to distinguish one bond from two bond scission.<sup>5</sup> Bridgehead vinyl groups, on the other hand, caused a large rate acceleration and led us to suggest

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concerted but asynchronous C-N cleavage for 3.6 The exocyclic cyclopropyl group of 7 decreased its thermal stability by more than 20 kcal mol<sup>-1</sup> while the endo cyclopropyl ring of 6 actually seemed to stabilize this compound relative to 5.

The present study encompasses five DBO derivatives (8-12)



and seeks to explore further the effect of structure on reactivity. Bridgehead methyl groups diminish the ground-state strain of DBO, accounting in part for their unusually small rate-accelerating effect. Because cyclopropyl groups provide a greater rate enhancement than that of methyl, we have been able to show that the results for 8 and 9 are perfectly consistent with synchronous C-N bond cleavage but not with a simple stepwise mechanism. If the first C-N bond homoloysis is reversible however, one can explain the data but cannot extract unique values for the three activation energies involved. The rate-enhancing effect of one bridgehead phenyl is much greater than that of the second such group. These results can be explained in terms of More O'Ferrall-Jencks-Thornton diagrams as asynchronous cleavage of 10 or as reversible, stepwise C-N homolysis. The phenyl substituents of 10 and 11 are not as effective rate accelerators as vinyl (3 and 4), in accord with the now recognized lower resonance stabilization energy (RSE) of benzyl than that of allyl radicals. Finally, compound 12 provides a more direct comparison with 7 than does the previously employed 6. The data for this DBO and for others from the literature reveal that endocyclic fused rings slow down thermolysis.

#### Synthesis of DBO Derivatives

The preparation of 8-11 was based on the usual triazolinedione route,<sup>5,6</sup> from the appropriate 1,3-cyclohexadienes. Diene 13 was



made by elimination<sup>9</sup> of the tosylhydrazone of enone 14.<sup>10</sup> Addition of cyclopropyllithium to cyclohexane-1,4-dione afforded 15, which was dehydrated with  $POCl_3$  in pyridine to 16.<sup>11</sup> Diene

Table I. Rate Constants for Thermolysis of DBO Derivatives<sup>a</sup>

compd	T, °C	$10^4 k$ , s <sup>-1</sup>	
DBO	230.05	0.583	
8	230.05	2.49	
9	230.05	10.7	
8	220.02	0.741	
	227.22	1.39	
	234.72	2.80	
	238.89	4.04	
10	157.33	1.06	
	165.16	2.18	
	180.33	8.41	
11 <sup>b</sup>	120.0	1.38	
12	239.0	0.521	
	244.2	0.796	
	249.0	1.18	
	253.6	1.90	

a By	UV spectroscopy	of 0.01	М	solutions	in	degassed	hexade-	
cane.	<sup>b</sup> In xylene.							

Table II. Activation Parameters for Thermolysis of DBO Derivatives

	$\Delta H^{\ddagger}$ ,		$\Delta G^{\ddagger}$ ,		
compd	mol <sup>-1</sup>	$\Delta S^{\pm}$ , eu	mol <sup>-1</sup>	$T^a$	ref
DBO	43.5 ± 0.03	8.4 ± 0.1	39.2	240	4
	$45.0 \pm 0.2$	$10.6 \pm 0.4$	39.6	240	5
			40.5	150	5
			40.8	120	5
1	$43.95 \pm 0.5$	$10.0 \pm 1.0$	38.8	240	5
2	$43.7 \pm 0.4$	11.4 ± 0.9	37.9	240	5
3	$34.2 \pm 0.8$	$7.7 \pm 2.0$	30.9	150	6
4	$28.8 \pm 0.3$	$1.5 \pm 0.8$	28.2	150	6
5	38.5	11.3	32.7	240	7
6	41.9 ± 1.4	$12.7 \pm 3.2$	35.4	240	7
7	$21.6 \pm 0.4$	$4.1 \pm 1.1$	20.0	120	8
8	$45.2 \pm 0.8$	$13.2 \pm 1.5$	38.4	240	this work
10	$34.1 \pm 0.2$	$1.7 \pm 0.4$	33.4	120	this work
11			30.2	120	this work
12	45.9 ± 2.0	$10.4 \pm 3.8$	40.6	240	this work

<sup>a</sup> Temperature (°C) at which the calculated  $\Delta G^{\ddagger}$  applies.

17 was made according to the literature procedure<sup>12</sup> while compound 11 was a gift.<sup>13</sup> The synthesis of 12 was achieved by 1,3-dipolar cycloaddition of diazomethane to the known azoxy compound 1814 followed by photochemical deazatization and



lithium aluminum hydride reduction. In contrast to the extremely low reactivity of ethyl azodicarboxylate and N-methyltriazolinedione adducts of dienes toward diazomethane, 18 was converted rapidly to a mixture of 19 and 20. The presence of seven pairs of <sup>13</sup>C peaks made it apparent that we were dealing with a mixture of isomers, but the complete absence of  $exo-21^{14}$  among the deazatization products showed that 1,3-dipolar cycloaddition

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We thank Professor Graham R. Underwood for providing a sample.

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Table III. Heats of Formation of Azoalkanes

compd	$\Delta H_{f}(g)$ , kcal mol <sup>-1</sup>
azo-2-propane (AIP) azo-2-methyl-2-propane (ATB) DBO 2	$\begin{array}{c} 8.51 \pm 0.85 \\ -8.70 \pm 0.66 \\ 40.32 \pm 0.39 \\ 22.1 \pm 1.1 \end{array}$

had produced only endo adducts 19 and 20. Both the rapid rate of cycloaddition and the exclusive endo stereochemistry suggest an activating effect of the azoxy moiety.

### **Results and Discussion**

Rate constants for thermolysis of compounds 8-12 are shown in Table I while activation parameters for these and other DBO derivatives from the literature are summarized in Table II. The 0.8 kcal mol<sup>-1</sup> decrease in  $\Delta G^{\ddagger}$  caused by each added bridgehead methyl group is considerably below the  $\sim 2.5$  kcal mol<sup>- $\bar{1}$ </sup> value found in acyclic azoalkanes.<sup>5</sup> If one looks at rate constants,  $k_{\rm rel}$ for DBO, 1, and 2 is 1.0, 2.13, and 5.06, respectively, at 239.93 °C whereas the acyclic series exhibits about a 15-fold acceleration per methyl group. It was not possible in the earlier work<sup>5</sup> to discern whether the thermolysis transition state of DBO was less stabilized by methyl groups than in the acyclic cases or whether these groups caused an extra lowering of the DBO ground-state energy. In an effort to resolve this question, we have now determined the heat of formation of DBO. This result and others selected from the literature<sup>1</sup> (cf. Table III) can be used to calculate the required differences in strain energy (S) by group additivity. In the case of DBO, we have  $\Delta H_f(DBO) = 4CH_2 + HC - N = N - CH +$ N=N-CH + S(AIP). Substracting the second equation from the first gives  $4CH_2 - 4CH_3 + S(DBO) - S(AIP) = \Delta H_f(DBO)$  $-\Delta H_{\rm f}({\rm AIP}) = 31.81$  kcal mol<sup>-1</sup>. A similar treatment of 2 and ATB leads to  $4CH_2 - 4CH_3 + S(2) - S(ATB) = \Delta H_f(2) - \Delta H_f(ATB) = 30.8 \text{ kcal mol}^{-1}$ . Again substracting the second equation from the first cancels the group values for CH<sub>2</sub> and CH<sub>3</sub>, giving  $[S(DBO) - S(2)] + [S(ATB) - S(AIP)] = 1.0 \pm 1.6$  kcal mol<sup>-1</sup>. If ATB and AIP are unstrained (or equally strained), DBO is more strained than 2 by 1 kcal  $mol^{-1}$ , but with a large uncertainty. This uncertainty is hardly surprising when one considers that we are in essence substracting two large, similar combustion heats. As an independent check, the heats of decomposition  $(\Delta H_r)$ of DBO and 2 were determined by differential scanning calorimetry (DSC). The difference between the two  $\Delta H_r$ 's was in excellent agreement with that calculated from the combustion  $\Delta H_{\rm f}$ 's (Table III) and group additivity  $\Delta H_{\rm f}$ 's of the product dienes. The results are summarized in the following equations:

SC: DBO (1, 297 °C) 
$$\rightarrow$$
  
22 (1, 207 °C)  $\downarrow$  N ( $\Rightarrow$  207 °C) 14.26 kg

**22** (l, 297 °C) +  $N_2$  (g, 297 °C) – 14.36 kcal mol<sup>-1</sup> DBO (g, 25 °C)  $\rightarrow$ 

**22** (g, 25 °C) +  $N_2$ (g, 25 °C) - 20.14 kcal mol<sup>-1</sup>

DSC: 2 (1, 272 °C) 
$$\rightarrow$$
  
23 (1, 272 °C) + N<sub>2</sub> (g, 272 °C) - 12.90 kcal mol<sup>-1</sup>

bomb:

bomb:

D

Calculated  $\Delta H_{f}$ 's of the two product dienes are given above. The discrepancy between the DSC and bomb values arises because DBO and 22, for example, have different heat capacities and heats



of vaporization. However, these differences tend to cancel when two similar reactions are compared. Because both DSC and bomb calorimetry indicate that DBO decomposes with 1.5 kcal mol<sup>-1</sup> greater exothermicity than 2 does, the  $\Delta H_{\rm f}$ 's in Table III gain



Figure 1. Ground- and transition-state enthalpies of formation ( $\Delta H_{\rm f}$ , kcal mol<sup>-1</sup>) of AIP, ATB, DBO, and 2.

support and we can conclude (a) that DBO is slightly more strained than 2 and (b) that ATB and AIP are unstrained or equally strained. Figure 1 shows how the ground and transition states for thermolysis are disposed. It appears that both of the effects considered initially are at work: methyl groups stabilize ground-state DBO and they lower the thermolysis transition state by an amount less than that in the acyclic series.

Although the DSC experiments argue against it, the equation  $[S(DBO) - S(2)] + [S(ATB) - S(AIP)] = 1.0 \text{ kcal mol}^{-1} \text{ could}$ also be accommodated if ATB were 1 kcal mol<sup>-1</sup> more strained than AIP while DBO and 2 were equally strained. However, the difference between ATB and AIP cannot exceed 1 kcal mol<sup>-1</sup> because the preceding equation would require 2 to be more strained than DBO. The latter is unlikely in view of the fact that added methyl groups are known to stabilize adamantane<sup>15</sup> and bicyclo[2.2.0] hexane.<sup>16</sup> Thus the 4.6 kcal mol<sup>-1</sup>  $\Delta H^*$  difference between AIP and ATB is not readily explained as a ground-state effect.<sup>17</sup> Some doubt has been expressed<sup>18</sup> about the activation parameters for AIP thermolysis, but the value shown in Figure 1 is close to that for azo-2-butane.<sup>19</sup> Data for azotoluenes further support the large magnitude of the  $\alpha$ -methyl effect in acyclic azoalkanes.5

If allowance is made for the differing ground-state energies of DBO and 2, a pair of methyl groups is found to stabilize the bicyclic transition state by 1.3 kcal mol<sup>-1</sup> vs. 4.6 kcal mol<sup>-1</sup> in the acyclic series. Which of these figures is "normal"? Recent data<sup>20,21</sup> suggest that tertiary radicals are 2.2 kcal mol<sup>-1</sup> lower in energy than secondary. Since the azoalkane thermolysis transition state is late,<sup>17</sup> the difference between  $\Delta H^{*}$  for AIP and ATB could be as much as  $2 \times 2.2 = 4.4$  kcal mol<sup>-1</sup>. The effect of radical stabilizing substituents supports a late transition state. As will be shown below, about half of the total available benzyl and allyl

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 (18) McMillen, D. F.; Lewis, K. E.; Smith, G. P.; Golden, D. M. J. Phys. Chem. 1982, 86, 709. The possibility that trans-cis isomerization is rate determining is criticized because the trans-cis isomerization rate obtained at 590 °C is 10 times faster than the rate calculated from activation parameters determined at 140 °C. In view of the  $\pm 2.9$  kcal mol<sup>-1</sup> error in the reported  $\Delta H^*$  and the 450 °C extrapolation, this criticism does not seem well founded.

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Table IV. Free Energy Increments for Bridgehead Substituents

group	$\Delta \Delta G_1^{\pm a}$	$\Delta\Delta G_2^{\pm b}$	T, ℃	
methyl cyclopropyl phenyl	0.8 1.4 7.4	0.9 1.5 3.2	240 230 120	
vinyl	9.6	2.7	150	

<sup>a</sup> Free energy decrease (kcal mol<sup>-1</sup>) relative to DBO caused by introducing one bridgehead group. <sup>b</sup> Free energy decrease caused by adding a second group.

RSE is manifested in the transition state for symmetrical azoalkane thermolysis. The transition state for AIP and ATB must be later than that of compounds yielding delocalized radicals because the former represent more endothermic reactions. Thus one might expect a  $\Delta H^*$  difference between secondary and tertiary azoalkanes close to 4.4 kcal mol<sup>-1</sup>, in agreement with the observed 4.6 kcal mol<sup>-1</sup> (Figure 1). The acyclic azoalkanes therefore behave normally while DBO's are unusually insensitive to  $\alpha$ -methylation. Lacking a better explanation, we have postulated unfavorable hyperconjugation in the developing radical sites as DBO decomposes.5

The rate constants shown in Table I for DBO, 8, and 9 are in the ratio 1.0:4.27:18.4. If *n* represents the rate enhancement for the first substituent, irreversible stepwise C-N bond breaking predicts a rate ratio of 1.0:n:2n-1 while concerted bond rupture predicts  $1.0:n:n^2$ . The observed values are in excellent agreement with the concerted mechanism. Thermolysis is accelerated only slightly by an  $\alpha$ -cyclopropyl group, in accord with its small stabilization of a radical center.<sup>22</sup> In comparison with the 18-fold rate enhancement from DBO to 9, 24 decomposes 9-times faster



than 25.23 However, thermolysis of 25 may already be facilitated by ground-state strain arising from the isopropyl groups.

Table IV presents the results for thermolysis of substituted DBO's in a manner that we have used previously.<sup>1,5</sup> The effect of the first and second substituent is shown as successive decreases in  $\Delta G^*$  for thermolysis. The temperature in these  $\Delta T^*$  comparisons is chosen to lie near the middle of the range used for thermolysis studies. In the case of phenyl, however, we had sufficient material<sup>13</sup> for only one kinetic run at 120 °C, so the activation parameters for DBO and 10 were extrapolated to this temperature. It is apparent that incorporation of two methyls or cyclopropyls has twice the effect of one such substituent. In contrast, the data for phenyl and vinyl substituents show the first bridgehead group to be much more influential than the second. Moreover, the difference between  $\Delta \Delta G_1^*$  and  $\Delta \Delta G_2^*$  grows larger in the better radical-stabilizing substituent, vinyl. The magnitude of these  $\Delta\Delta G^*$ 's is close to the values for acyclic azoalkanes (7.8, 3.4 kcal mol<sup>-1</sup> for phenyl and 9.6, 2.4 kcal mol<sup>-1</sup> for vinyl at 80 °C).1

One rationalization of the foregoing results is based upon Figure 2, a More O'Ferrall-Jencks-Thornton diagram.<sup>24</sup> When the azoalkane is unsymmetrical, the transition state (\* in Figure 2) is characterized by much more stretching of the C-N bond to the incipient allylic radical than of the C-N bond to the secondary radical. Thus the transition state becomes unsymmetrical and lowers its energy by partaking of the incipient allylic resonance.



Figure 2. More O'Ferrall-Jencks-Thornton diagram for thermolysis of an unsymmetrical azoalkane. The transition state is marked \*, and its projection onto the two C-N bond breaking axes shows more advanced cleavage of the weaker bond.

With such an unsymmetrical transition state, little is to be gained by making the second radical allylic so that  $\Delta \Delta G_2^*$  is less than  $\Delta \Delta G_1^*$ . A single weak substituent like methyl leaves the transition state essentially symmetrical; hence, the help provided by a second methyl is comparable to  $\Delta \Delta G_1^*$ . These effects are apparent in Table IV.

The stabilization afforded by two phenyl groups  $(\Delta \Delta G_1^* +$  $\Delta\Delta G_2^*$ ) is 10.6 kcal mol<sup>-1</sup> while the value for two vinyls is 12.3 kcal mol<sup>-1</sup>. Although these results are in good accord with the most recent determinations of the benzyl and allyl RSE's (10.2 and 11.9 kcal mol<sup>-1</sup>, respectively),<sup>21</sup> they are inconsistent with the values generally accepted in 1973 (13.9 and 9.6 kcal mol<sup>-1</sup>).<sup>25</sup> It is amusing that the correct ordering of these RSE's has been available for years from thermolysis rates of acyclic and monocyclic azoalkanes.<sup>26</sup> If the simultaneous scission mechanism is correct, the fact that only one benzyl or allyl RSE ( $\sim 11$  kcal mol<sup>-1</sup>) is manifested in thermolysis of symmetrical azoalkanes suggests that the two C-N bonds are each about half broken at the transition state.

Recent work in this laboratory<sup>27</sup> has shown that in acyclic (dimethylallyl)azoalkanes 26, the amount of 27 decreases as R



is changed to a more stable radical. Although we would not expect allylic recombination in 3 or 4 because of a Bredt's rule violation, the results in the acyclic series force us to consider a reversible, stepwise cleavage mechanism for DBO's. The transition state for concerted cleavage (\* in Figure 2) would be at high energy and the decomposition would proceed via the left, front corner. Although kinetics of azoalkane disappearance cannot provide enough information to determine all of the desired activation energies, a few quantitative statements can be made. The apparent activation free energy for stepwise cleavage equals  $\Delta G_a^* - \Delta G_b^* +$  $\Delta G_c^*$  where a, b, and c refer to the steps below. For a series such



as DBO, 3, 4, there will be three observable quantities and nine unknown activation energies. Let  $G_{a1}$ ,  $G_{b1}$ , and  $G_{c1}$  be the  $\Delta G^{*}$ 's for DBO in reactions a, b, and c and then similarly define  $G_{a2}$ - $G_{c3}$ for the reactions below. Adding 0.6 kcal mol<sup>-1</sup> to the observed  $\Delta G^*$  for DBO and 4 corrects for their statistical rate factor of

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(23)</sup> Martin, J. C.; Timberlake, J. W. J. Am. Chem. Soc. 1970, 92, 978.
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Row: New York, 1981; p 201.

<sup>(25)</sup> O'Neal, H. E.; Benson, S. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; p 285.

<sup>(26)</sup> Pyrazolines yield a  $\Delta G^*$  difference between two phenyls and two vinyls closer to the 1.7 kcal mol<sup>-1</sup> found here than do the acyclic azoalkanes, where the difference is 0.3-0.8 kcal mol<sup>-1</sup>

<sup>(27)</sup> Engel, P. S.; Gerth, D. B. J. Am. Chem. Soc. 1983, 105, 6849.



2 at 150 °C due to two equivalent C-N bonds and allows us to write the following equations.

$$G_{al} - G_{bl} + G_{cl} = 41.1$$
  

$$G_{a2} - G_{b2} + G_{c2} = 30.9$$
  

$$G_{a3} - G_{b3} + G_{c3} = 28.8$$

It is likely that  $G_{a2} = G_{a3}$ ,  $G_{b2} = G_{b3}$ , and  $G_{c1} = G_{c2}$  because the same kinds of bonds are involved. Assuming that  $G_{c3}$  is negligible because this step should be highly exothermic, we conclude that  $G_{c1}$  is 2.1 kcal mol<sup>-1</sup> and that  $G_{a1} - G_{b1} = 39.0$  kcal mol<sup>-1</sup>. If diazenyl-alkyl and diazenyl-allyl recombination proceed with the same barrier,  $G_{b1} = G_{b2}$  and  $G_{a1} - G_{a2} = 10.2$  kcal mol<sup>-1</sup>. This activation energy difference is 86% of the most recent allyl resonance energy.<sup>21</sup> In order to obtain the full allyl resonance energy (11.9 kcal mol<sup>-1</sup>),  $G_{b1}$ - $G_{b2}$  would have to be 1.7 kcal mol<sup>-1</sup>; that is, diazenyl-allyl recombination must possess a smaller barrier than diazenyl-alkyl recombination. A similar treatment with the bridgehead phenyl compounds at 120 °C gives  $G_{c1} = 2.7$ ,  $G_{a1} G_{b1} = 38.6$ , and  $G_{a2} - G_{b2} = 30.7$  kcal mol<sup>-1</sup>. If  $G_{b1} = G_{b2}$ , then  $G_{a1} - G_{a2} = 7.9$  kcal mol<sup>-1</sup> or 77% of the benzyl resonance energy.<sup>21</sup> The values of  $G_{c1}$  obtained from the two sets of compounds are reasonably consistent and indicate that the alkyldiazenyl intermediate must surmount a small barrier before losing nitrogen. If  $G_{c1}$  also equals 2.3 kcal mol<sup>-1</sup> for the cyclopropyl (8, 9) and methyl (1, 2) series of DBO's,  $G_{c3}$  comes out 1.5 and 2.1 kcal mol<sup>-1</sup>, respectively. By comparison,  $G_{c3}$  for tert-butyldiazenyl radical was recently estimated as 2.2 kcal mol<sup>-1,27</sup>

Abandoning our initial assumption of  $G_{c3} = 0$  for 4 and 11 will raise  $G_{c1}$ ; in fact, it has been calculated<sup>28</sup> that the barrier to deazatization of ethyldiazenyl radical is 14 kcal mol<sup>-1</sup>. Unfortunately, our ignorance of  $G_{c3}$ ,  $G_{b1}$ , and  $G_{b2}$  prevents us from determining all of the desired  $\Delta G^*$ 's. Another problem with this approach is the fact that  $\Delta S^{\dagger}$  varies widely in a series like DBO, 3, and 4, thereby making  $\Delta\Delta G^*$  a function of temperature. With only reaction rates as a tool, there is little else one can do to decide between reversible stepwise and simultaneous C-N bond homolysis. Further progress will require spectroscopic or at least indirect monitoring of diazenyl radicals.

Allred and Hinshaw<sup>29</sup> discovered in 1969 that deazatization was accelerated enormously by an exo-fused cyclopropane ring (7) but not as much by an exo cyclobutane (5). The additional conclusion that an endo cyclopropyl group produced no acceleration was based on the rate constants for 6 because 12 was unknown at the time. The present data for 12 confirm what was indicated by 5 and 6, namely, that an endo cyclopropyl actually stabilizes the azoalkane. A possible explanation is that the planarity, which seems to be required at the  $\alpha$ -carbons during C-N bond breaking,<sup>30</sup> forces the departing nitrogen into close proximity to the cyclopropane ring. The as yet unknown endo isomer of 5 should exhibit similar behavior.

The stabilizing effect of endocyclic fused rings is also seen in compound **28** ( $\Delta G^*(120 \text{ °C}) = 32.6 \text{ kcal mol}^{-1})^{31}$  which is more stable than 11; on the other hand, 29 ( $\Delta G^*(135 \text{ °C}) = 30.2 \text{ kcal}$  $mol^{-1}$ )<sup>32</sup> is of the same stability as 11. It seems unwise to interpret



these results too closely, for 28 has an unusually negative  $\Delta S^*$ while only one crude kinetic run was reported for 29.

In summary, thermolysis of DBO derivatives is accelerated less by bridgehead methyl groups but to the same degree by radical-delocalizing substituents as are acyclic azoalkanes. Concerted, asynchronous C-N bond scission or a reversible, stepwise mechanism will explain these effects equally well. As expected from the larger resonance stabilization energy of allyl than that of benzyl,  $\alpha$ -vinyl substitution enhances the rate more than  $\alpha$ -phenyl groups. Endocyclic fused rings render DBO's more stable, probably by preventing the planarity of the  $\alpha$ -carbon that is required for departure of nitrogen.

# **Experimental Section**

Melting points were taken on a Mel-Temp in capillary tubes and are uncorrected. NMR spectra were recorded in CDCl<sub>3</sub> on a Varian EM390 or a Jeol FX90Q FT spectrometer while UV spectra were taken on a Cary 17 spectrometer. A CEC 21-110B mass spectrometer was used to obtain exact masses.

Synthesis of Azoalkanes. 1-Cyclopropyl-1,3-cyclohexadiene (13). A solution of 10.2 g 3-cyclopropylcyclohex-2-enone (14),<sup>10</sup> 15.9 g ptoluenesulfonylhydrazide, and 3 drops of concentrated HCl in 200 mL THF was refluxed under N<sub>2</sub> for 16 h through a Soxhlet extractor containing 4-Å molecular sieves. The solution was cooled to 0 °C and 140 mL of 1 M MeLi in ether was added dropwise. The resultant dark red solution was stirred at 0 °C for 3 h, warmed to room temperature, and stirred for an additional 1.5 h. After slow addition of 200 mL of H<sub>2</sub>O and vigorous stirring for 1 h, the solution was extracted with  $3 \times 150$  mL portions of pentane. The combined pentane fractions were dried over MgSO4 and filtered. This solution was normally used directly in the next step; however, a pure sample of 1-cyclopropyl-1,3-cyclohexadiene was obtained by rotoevaporation of the solvent and vacuum distillation through a short column containing glass helices: bp 42-45 °C (2 mm), NMR δ 0.38-0.75 (m, 4 H), 1.22-2.60 (m, 1 H), 2.80-3.32 (m, 4 H), 5.51-6.00 (m, 3H); calcd for C<sub>9</sub>H<sub>12</sub> (M<sup>+</sup>·), m/e 120.0939; found, m/e120.0940; calcd  $(M^+ - H_2)$ , m/e 118.0783; found, 118.0780.

1-Cyclopropyl-4-methyl-2,4,6-triazatricyclo[5.2.2.0<sup>2,6</sup>]undec-8-ene-3,5dione. To the crude diene solution obtained above was added a solution of N-methyltriazolinedione (MTD) in EtOAc<sup>6</sup> until the red color of the MTD barely persisted. The solution was filtered and concentrated. The resulting yellow crystals were recrystallized from acetone to yield 5.5 g (31.6% from 14) of adduct as white crystals: mp 110.5-113 °C; NMR δ 0.32-0.90 (m, 4 H), 1.23-2.31 (m, 5 H), 3.00 (s, 3 H), 4.84 (br s, 1 H), 5.92-6.49 (m, 2 H); calcd for  $C_{12}H_{15}N_3O_2$  (M<sup>+</sup>·); m/e 233.1164; found. 233.1167.

1-Cyclopropyl-4-methyl-2,4,6-triazatricyclo[5.2.2.0<sup>2,6</sup>]undecane-3,5dione. To a stirred solution of the above adduct (8.1 g) in 150 mL of absolute EtOH was added a small portion of Norite. After 15 min, the mixture was filtered through Celite. To the filtrate was added 500 mg of 10% Pd/C and the mixture was then hydrogenated at 1 atm (953 cm<sup>-1</sup> H<sub>2</sub> adsorbed). The solution was filtered through Celite and concentrated to yield 7.6 g (93.0%) of product as white crystals: mp 83-85 °C; NMR δ 0.36-0.74 (m, 4 H), 1.52-2.12 (m, 9 H), 3.09 (s, 3 H), 4.35 (br s, 1 H); calcd for  $C_{12}H_{17}N_3O_2$  (*M*<sup>+</sup>·), *m/e* 235.1321; found, 235.1314.

1-Cyclopropyl-2,3-diazabicyclo[2.2.2]oct-2-ene (8). A solution of 7.6 g of the above hydrogenated adduct and 16.5 g KOH in 250 mL of i-PrOH was refluxed under N2 for 15 h. The cooled mixture was filtered and the solids were washed with several portions of MeOH. The combined filtrate and washings were rotoevaporated, yielding a yellow oil. The oil was dissolved in 200 mL of H<sub>2</sub>O and extracted with 200 mL of  $CH_2Cl_2$ . The  $CH_2Cl_2$  layer was then washed with 3 × 50 mL portions of H2O, dried over MgSO4, and filtered. The CH2Cl2 was rotoevaporated to yield 2.9 g of crude yellow crystals. Recrystallization from pentane at -78 °C afforded 2.0 g (41.2%) of 8 as white crystals: mp 49.5-52.5 °C; NMR  $\delta$  0.48–2.72 (m, 13 H), 5.12 (br s, 1 H); calcd for C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>, m/e 150.1157; found, 150.1159; calcd (M<sup>+</sup> - N<sub>2</sub>), m/e 122.1096; found, 122.1096. Further purification of 8 was accomplished by two successive sublimations followed by low-temperature recrystallization from pentane.

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$AU = 9424.29 + 2.02$ col $a^{-1}$ (overage of 9 muns)
$\Delta U_{\rm c} = 8454.56 \pm 2.92$ cal g = (average of 6 runs)
$\Delta H_{c} = 930.61 \pm 0.32 \text{ kcal mol}^{-1}$
$\Delta H_{f}(s) = 24.71 \pm 0.37 \text{ kcal mol}^{-1}$
$\Delta H_{\rm v} = 15.61 \pm 0.13 \text{ kcal mol}^{-1}$
$\Delta H_{f}(g) = 40.32 \pm 0.39 \text{ kcal mol}^{-1}$
$C_p(25 ^{\circ}\text{C}) = 36.1 \text{eu}$
density = $1.268 \text{ g/cm}^3$
purity of sample = 99.98%
mp = 144.1 °C; $\Delta H_{fusion} = 1.16 \text{ kcal mol}^{-1}$
phase transition at 78.8 °C; $\Delta H = 1.95$ kcal mol <sup>-1</sup>

1-Phenyl-4-methyl-2,4,6-triaza[5.2.2.0<sup>2,6</sup>]tricycloundec-8-ene-3,5-dione. 1-Phenylcyclohexa-1,3-diene (17) was prepared according to the literature procedure.<sup>12</sup> In a 100-mL round-bottom flask equipped with an addition funnel and stirring bar was placed 2.38 g (15.2 mmol) of 17 in 40 mL of EtOAc. N-Methyltriazolinedione solution<sup>6</sup> was added dropwise at 25 °C until an excess was indicated by the persistence of a slight red color. The solvent was removed by rotoevaporation and the solid was recrystallized from EtOAc; yield, 1.86 g (44.1%) of a white solid: mp 184-185 °C; NMR  $\delta$  1.50-1.72 (m, 2 H), 2.28-2.50 (m, 2 H), 2.92 (s, 3 H), 5.00 (br s, 1 H), 6.58 (d of d, 1 H, J = 8, 6 Hz), 7.02 (d, 1 H, J= 8 Hz), 7.52 (m, 5 H).

1-Phenyl-4-methyl-2,4,6-triaza[5.2.2.0<sup>2.5</sup>]tricycloundecane-3,5-dione. In a 250-mL round-bottom flask was placed 1.80 g (6.7 mmol) of the above adduct and 50 mg of 10% Pd/C in 200 mL of THF. The mixture was hydrogenated at 1 atm at 25 °C until H<sub>2</sub> absorption ceased. The solution was filtered and concentrated; yield; 1.82 g (100%). A sample recrystallized from EtOAc had mp 201-202 °C; NMR  $\delta$  1.60-2.6 (m, 8 H), 3.01 (s, 3 H), 4.42 (br s, 1 H), 7.1-7.6 (m, 5 H); calcd for C<sub>15</sub>-H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>, *m/e* 271.1321 (*M*<sup>+</sup>); found, *m/e* 271.1317.

1-Phenyl-2,3-diazabicyclo[2.2.2]oct-2-ene (10). A dry 100-mL three-necked flask equipped with a reflux condenser, N2 inlet, addition funnel, and a magnetic stirring bar was charged with 60 mL of *i*-PrOH (previously distilled from CaO). To this was added 4.2 g (0.064 mol) of solid KOH (85% purity) and 1.75 g (6.45 mmol) of the hydrogenated adduct. The mixture was heated at reflux for 18 h under N2. The cooled reaction mixture was filtered and the solids were washed with CH<sub>2</sub>Cl<sub>2</sub>. The combined filtrates and washings were rotoevaporated to dryness, yielding a white semisolid. This was dissolved in 100 mL of water and neutralized to pH 7 with 1 N HCl. The aqueous solution was extracted three times with CH<sub>2</sub>Cl<sub>2</sub> and dried over K<sub>2</sub>CO<sub>3</sub>. After rotoevaporation of the solvent, the resulting N-methylurea was dissolved in i-PrOH and added dropwise to 50 mL of a 0.82 M CuCl<sub>2</sub> solution. A brick-red precipitate slowly formed. The mixture was stirred for 2 h and then filtered, yielding 0.506 g of the cuprous chloride complex of 10. The complex was added in portions to a heterogeneous mixture of 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and 50 mL of concentrated NH<sub>4</sub>OH. This mixture was stirred for 30 min, and the aqueous layer was extracted three times with CH<sub>2</sub>Cl<sub>2</sub> and dried with MgSO<sub>4</sub>. Rotoevaporation of the solvent yielded 0.314 g of crude 10. Following sublimation and recrystallization from hexanes, 0.284 g of (23.6% yield) white needles were obtained: mp 110-111 °C; NMR  $\delta$  1.20–2.20 (m, 6 H), 5.29 (br s, 1 H), 7.25–7.84 (m, 5 H).

**1,4-Diphenyl-2,3-diazabicyclo[2.2.2]oct-2-ene** (11)<sup>13</sup> gave UV ( $C_6H_6$ )  $\lambda_{max}$  386 nm ( $\epsilon$  133); NMR ( $C_6D_6$ )  $\delta$  1.46 (m, 8 H), 7.72 (m, 10 H); mp 180 °C dec.

endo -2,3-Diazatricyclo[3.2.2.0<sup>5,7</sup>]non-2-ene (12) was prepared in a three-step sequence from 2,3-diazabicyclo[2.2.2]octa-2,5-diene N-oxide (18). The literature procedure<sup>14</sup> for 18 was improved by adding the KOH solution and the 30% H<sub>2</sub>O<sub>2</sub> simultaneously from different dropping funnels. This method not only avoided a violent exothermic reaction but also raised the yield to 88% (lit.<sup>14</sup> 70\%).

endo-2,3,6,7-Tetraazatricyclo[5.2.2.0<sup>5,9</sup>]undeca-2,6-diene 2-Oxide (19 and 20). A solution of diazomethane was generated from 9.3 g of nitrosomethylurea.<sup>33</sup> The diazomethane solution was partitioned among three pressure bottles (100-mL capacity), each of which contained 2.0 g (16 mmol) of 18 in 20 mL of ether. The bottles were capped and the contents stirred. Soon the heterogeneous mixture became homogeneous and then turned cloudy with the separation of a pale yellow oil. Stirring was continued overnight. The bottles were then cooled to -78 °C, and the ether layer was decanted from the oil or semisolid product. Since the decanted ether layers consisted mainly of unreacted starting material, nitrogen was bubbled through to remove the excess diazomethane. The solvent was then rotoevaporated to recover **19** + **20** as a yellow oil, which was treated again with diazomethane as above. Purification of the combined crude product (9.05 g) was accomplished by chromatography on 300 g of Fluorisil (EtOAc eluent). Compounds **19** and **20** were obtained as a white powder: mp 85–94 °C (5.7 g, 71% yield); NMR  $\delta$  1.58–2.06 (m, 4 H), 2.06–2.67 (m, 1 H), 4.23–4.77 (m, 3 H), 5.05 (d, 1 H), 5.25–5.45 (m, 1 H); IR (KBr) 1495 cm<sup>-1</sup> (NNO); UV (EtOH)  $\lambda_{max}$  322 ( $\epsilon$  413), 230 ( $\epsilon$  6.79 × 10<sup>3</sup>); <sup>13</sup>C NMR  $\delta$  89.25, 88.77, 81.34, 79.56, 73.31, 71.47, 58.35, 57.40, 33.70, 30.93, 22.66, 21.79, 21.11, 20.32; calcd for C<sub>7</sub>H<sub>10</sub>N<sub>4</sub>O, *m/e* 166.0854; found, 166.0855.

endo-2,3-Diazatricyclo[3.2.2.0<sup>5,7</sup>]non-2-ene 2-Oxide (21). Into a 500-mL Pyrex photochemical reactor with a gas inlet was added 19 + 20 (2.54 g, 15.3 mmol) and 550 mL of acetonitrile. After purging with N<sub>2</sub>, irradiation of the solution for 6 h resulted in complete destruction of the azo chromophore. Rotoevaporation of solvent afforded 2.9 g of a pungent, orange oil. This oil was partially purified by chromatography (silica gel, EtOAc eluant) to yield 21 (1.28 g, 61%). This material showed several extra resonances in the olefinic region, but attempts to short path distillation failed. NMR  $\delta$  -0.10-0.18 (m, 1 H), 0.27-0.59 (q, 1 H), 1.17-1.50 (m, 2 H), 1.54-2.07 (m, 4 H), 4.50 (br s, 1 H), 4.72 (br s, 1 H).

endo-2,3-Diazatricyclo[3.2.2.05,7]non-2-ene (12). Azoxy compound 21 (1.00 g, 7.24 mmol), lithium aluminum hydride (750 mg, 20 mmol), and 110 mL of dry ether were added to a 250-mL flask fitted with a reflux condenser and nitrogen inlet. A mildly exothermic reaction ensued and the resulting brown, heterogeneous mixture was stirred for 2 h at reflux. Excess LAH was then decomposed by adding successive portions of 0.75 mL water, 0.75 mL of 15% aqueous NaOH, and 2.25 mL of water and stirring for 1 h. The white inorganic salts were filtered off, and 50 mg of 10% Pd/C was added to the ether filtrate. Bubbling oxygen through the solution for 20 min oxidized the hydrazine to 12. The solution was dried  $(K_2CO_3)$ , the catalyst filtered off, and the ether removed by rotoevaporation. Short-path microdistillation afforded crude 12 in 60% yield. The compound was purified further by preparative GC (5% SE-30, 5 ft  $\times$  0.375 in., oven 128 °C) to furnish 12 (118 mg, 13%) as a colorless oil: mp -2 to 0 °C; NMR  $\delta$  -0.27 to -0.11 (m, 1 H), 0.11-0.36 (q, 1 H), 1.03–1.93 (m, 6 H), 5.22 (br s, 2 H); UV (benzene  $\lambda_{max}$  379 ( $\epsilon$  214), 368 (sh) ( $\epsilon$  114); calcd for C<sub>7</sub>H<sub>10</sub>, m/e 94.0783; found; 94.0786 ( $M^+$ . - N<sub>2</sub>, no  $M^+$  peak seen).

**Kinetics** (0.01 M in degassed hexadecane) were obtained by monitoring the decrease in the azo chromophore by UV spectroscopy. Temperatures were measured with a platinum resistance thermometer, and the oil bath was regulated by a Bayley temperature controller. The only product from 12 was 1,4-cycloheptadiene, as shown by comparison with an authentic sample.

Combustion calorimetry was carried out as described previously.<sup>34</sup> Differential scanning calorimetry was done in high-pressure pans with a Mettler TA3000 system. The results of these and other measurements on DBO are summarized in Table V.

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**Registry No. 2**, 49570-30-1; **8**, 87373-47-5; **9**, 87433-32-7; **10**, 87373-48-6; **11**, 87433-33-8; **12**, 87420-89-1; **13**, 87433-34-9; **14**, 34194-40-6; **17**, 15619-32-6; **18**, 37436-17-2; **19**, 87433-39-4; **20**, 87433-40-7; **21**, 87480-67-9; AIP, 3880-49-7; DBO, 3310-62-1; MTD, 13274-43-6; ATB, 927-83-3; *p*-toluenesulfonylhydrazide, 1576-35-8; 1-phenyl-4-methyl-2,4,6-triaza[5.2.2.0<sup>2.6</sup>]tricycloundecane-3,5-dione, 87433-37-2; 1-cyclopropyl-4-methyl-2,4,6-triaza[5.2.2.0<sup>2.6</sup>]tricycloundec-8-ene-3,5-dione, 87433-37-2; 1-cyclopropyl-4-methyl-2,4,6-triaza[5.2.2.0<sup>2.6</sup>]tricycloundec-8-ene-3,5-dione, 87433-35-0; 1-cyclopropyl-4-methyl-2,4,6-triaza[5.2.2.0<sup>2.6</sup>]tricycloundec-8-ene-3,5-dione, 87433-36-1.

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