

oxydisulfate concentration was calculated by using the following equation:

$$[\text{S}_2\text{O}_8^{2-}] = \frac{(\text{coulombs})}{96.5(0.1)(2)}$$

Typical Procedure. The following example is typical of the general procedure used in the kinetic runs. Two stock solutions were freshly prepared: stock solution A, 0.02 M $\text{K}_2\text{S}_2\text{O}_8$ in 0.2 M KOH; stock solution B, 0.24 M 18-crown-6. A 50-mL aliquot of stock solution A was placed in a 250-mL round-bottomed 2-necked flask fitted with a thermometer and equilibrated in a constant temperature bath to 60 ± 0.1 °C. After equilibration to 60 °C a 50-mL aliquot of stock solution B was transferred to the flask, giving final concentrations of 0.12 M 18-crown-6 and 0.01 M $\text{K}_2\text{S}_2\text{O}_8$ in 0.1 M KOH. The flask was shaken to ensure good mixing, and a sample (about 0.5 mL) was withdrawn to mark zero time. Samples were then withdrawn periodically for analyses until 90–95% disappearance of peroxydisulfate. Upon withdrawal, each sample was

quenched by rapid cooling to 0 °C. Successive analyses showed no change in peroxydisulfate concentration at 0 °C over several hours.

UV Study. A typical run (0.01 M $\text{K}_2\text{S}_2\text{O}_8$, 0.02 M 18-crown-6 in 0.1 M KOH, 60 °C) was repeated. Samples were examined by recording spectra utilizing a Cary Model 14 spectrophotometer in the region 400–200 nm vs. a blank solution identical with the reaction mixture except that the peroxydisulfate was omitted.

Product Study. The reaction mixture following a kinetic run was continuously extracted with toluene for 2 days. The yellow residue obtained upon evaporation of the solvent displayed spectral properties very similar to those of 18-crown-6 with the following exceptions: IR (neat) 1700 cm^{-1} (weak absorption); NMR τ (Me_4Si , CDCl_3) -0.10 (s); comparison of the intensity of this aldehyde proton absorption to the intensity of the ^{13}C satellite peak of the crown ether methylenes allowed estimation of 13% aldehyde in the mixture.

Registry No. Potassium peroxydisulfate, 7727-21-1; 18-crown-6, 17455-13-9.

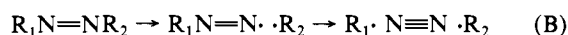
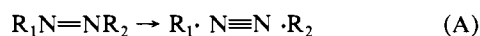
Thermolysis of Acyclic Azoalkanes: Simultaneous or Stepwise C–N Homolysis?

Paul S. Engel* and Dale B. Gerth

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77251. Received June 13, 1983

Abstract: Irradiation of several *trans*- α,α -dimethylallylazoalkanes produces the thermally labile *cis* isomers. Among their thermolysis products, we have found "turnaround" azoalkanes (TA) corresponding to recombination of alkyldiazanyl radicals ($\text{RN}=\text{N}\cdot$) at the primary end of the dimethylallyl radical. The amount of TA decreases when R \cdot is a better radical, suggesting a competition between β scission of $\text{RN}=\text{N}\cdot$ and recombination to give starting azoalkane and TA. A stepwise, internal-return mechanism correctly predicts when formation of TA will be important.

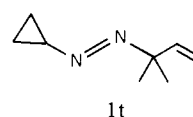
The mechanism by which azoalkanes lose nitrogen has been debated since Ramsperger¹ first posed the question in 1929 right up to the present day. Two mechanisms have received the most attention: simultaneous cleavage of both C–N bonds (A) and stepwise homolysis via a diazenyl radical (B). When the



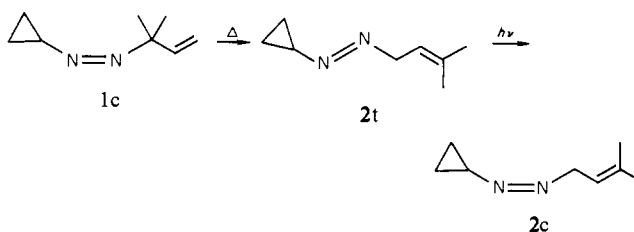
azoalkane is symmetrical, most of the previous evidence has favored (A),² but highly unsymmetrical azoalkanes (e.g., $\text{R}_1 = \text{Ph}$, $\text{R}_2 = \alpha,\alpha$ -dimethylallyl) clearly decompose via mechanism (B).³ Our assessment of the situation in 1980 was "azoalkane thermolysis seems to proceed by a continuum of mechanisms between (A) and (B); the more unsymmetrical the azo compound, the more unsymmetrically it cleaves".^{4,5} A recent MNDO calculation on azoethane⁶ and a solution-phase pressure study of azo-1-adamantane⁷ have led to the conclusion that even symmetrical

azoalkanes may decompose by stepwise homolysis. Presently, we report evidence for mechanism B with the first step reversible⁸ for thermolysis of *cis* and *trans* acyclic azoalkanes.

Irradiation of **1t**^{9,10} in C_6D_6 at 25 °C with a nitrogen laser (337



nm) produced two new azoalkanes (**2t** and **2c**) along with the usual



(1) Ramsperger, H. C. *J. Am. Chem. Soc.* **1929**, *51*, 2134.

(2) For the exception, see: Crawford, R. J.; Takagi, K. *J. Am. Chem. Soc.* **1972**, *94*, 7406. These results are consistent with the mechanism advocated here since internal return is absent in the gas phase. The thermolysis rate should therefore depend only on the strength of the weaker C–N bond.

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

(4) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

(5) On the basis of an elegant series of experiments, Seltzer expressed the same viewpoint 8 years earlier. Tsolis, A.; Mylonakis, S. G.; Nieh, M. T.; Seltzer, S. *J. Am. Chem. Soc.* **1972**, *94*, 829. See also: Hinz, J.; Oberlinner, A.; Ruchardt, C. *Tetrahedron Lett.* **1973**, 1975.

(6) Dannenberg, J. J.; Rocklin, D. *J. Org. Chem.* **1982**, *47*, 4529.

(7) Neuman, R. C.; Binegar, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 134.

(8) Reversible cleavage for phenylazotriphenylmethanes was first proposed by Pryor. See: Pryor, W. A.; Smith, K. *J. Am. Chem. Soc.* **1967**, *89*, 1741.

(9) Azocyclopropane was recently reported. Engel, P. S.; Gerth, D. B. *J. Am. Chem. Soc.* **1981**, *103*, 7689.

(10) Prepared by the method of: Baldwin, J. E.; Brown, J. E.; Hofle, E. *J. Am. Chem. Soc.* **1971**, *93*, 788.

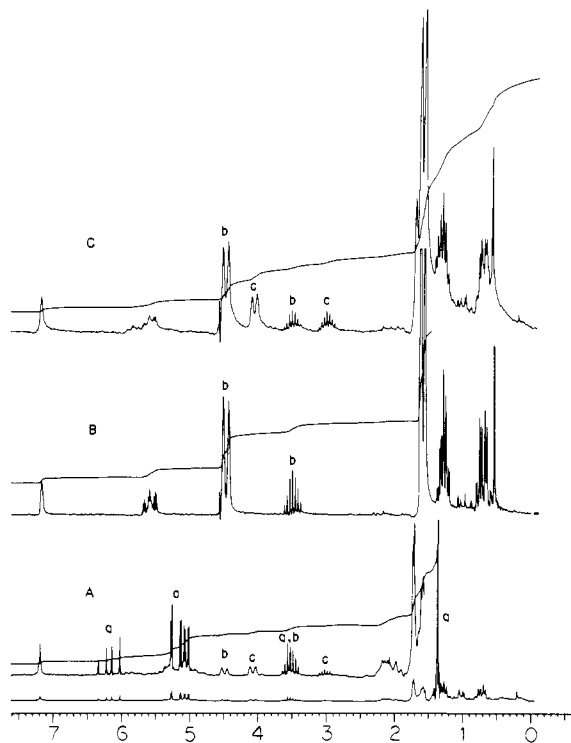


Figure 1. 90-MHz NMR spectra in C_6D_6 : (A) **1t** irradiated at 337 nm for 1 h; (B) **2t** isolated from irradiated **1t**. The tallest peaks are truncated to conserve space; (C) **2t** irradiated at 337 nm for 1 h. Characteristic peaks are marked as follows: **1t**-a, **2t**-b, **2c**-c.

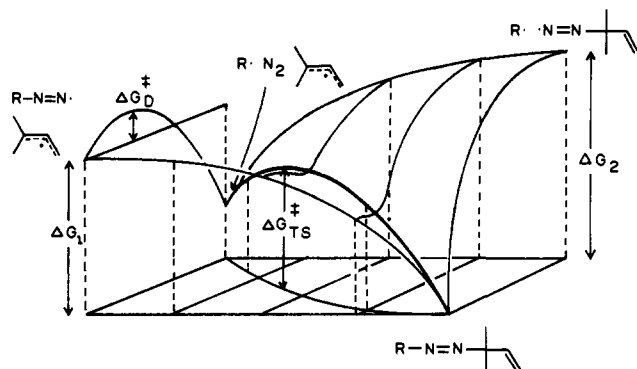
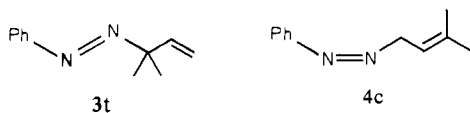


Figure 2. Possible decomposition pathways of dimethylallylazoalkanes. ΔG_{TS}^\ddagger is the activation barrier for concerted, asynchronous C-N cleavage while $\Delta G_I^\ddagger + \Delta G_D^\ddagger$ is the barrier to stepwise, reversible cleavage.

spectroscopy, as was done previously^{11,12} with very similar compounds.

Formation of TA is not new, for Porter observed the analogous product from **3t**.¹¹ Since the *cis* isomer (**4c**) was not mentioned,¹³ we irradiated **3t** and isolated both **4c** and its *trans* isomer. These



results indicate that diazenyl radical intermediates survive long enough to recombine at the primary end of the dimethylallyl radical. Although the existence of phenyldiazenyl might have been anticipated from the high C-H (and presumably C-N) bond dissociation energy of benzene (BDE = 111 kcal mol⁻¹), it was not obvious that cyclopropyldiazenyl would also exist (BDE(cy-

Table I. Detection of Turnaround Product from Irradiation of $RN=NCMe_2CH=CH_2$

R	compd	BDE (R-H) ^a	turnaround ^b	
			<i>trans</i>	<i>cis</i>
Ph	3	111	isol.	isol.
cyclopropyl	1	106.3	isol.	isol.
CH ₃	6	105.1	HPLC, NMR	(HPLC)
C ₂ H ₅	7	98.2	HPLC, NMR	
<i>i</i> -C ₃ H ₇	8	95.1	HPLC, NMR ^c	HPLC
1-adamantyl	9	94.4	(HPLC, NMR) ^d	
<i>t</i> -C ₄ H ₉	10	93.2	n.d.	n.d.
H ₂ C=CHCMe ₂	5	77.2	n.d.	n.d.

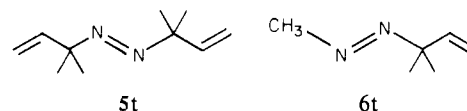
^a Bond dissociation energy (kcal mol⁻¹) from ref 15. ^b *isol.* = isolated; HPLC = detected by HPLC; NMR = detected by NMR; n.d. = not detected, even on irradiation at -78 °C. Parentheses mean that the signal was barely above the noise level. ^c Weak. ^d Only at -78 °C; none detected upon irradiation at 25 °C.

Table II. Quantum Yields for **1t**^a

solvent	% dec ^b	Φ_T^c	Φ_{TA}^d	$\Phi_{N_2}^e$	F_T^f
pentane	83.2	0.141	0.015	0.126	0.12
hexadecane	72.2	0.122 ^g	0.036	0.087	0.39

^a 400-min irradiation of a 0.435 M solution with 366-nm light of intensity of 0.192 einsteins per h. ^b Percent of **1t** decomposed. ^c Total quantum yield for disappearance of **1t**. ^d Formation of turnaround product **2t**. ^e Nitrogen quantum yield calculated as $\Phi_T - \Phi_{TA}$. ^f Φ_{N_2} measured directly was shown in an independent experiment to equal this difference. ^g Fraction of cyclopropyldiazenyl-dimethylallyl radical pairs that return to **1t** and **2t**. See text. ^h The same value was obtained at 39.2% conversion.

clopropyl-H) = 106.3 kcal mol⁻¹).¹⁴ Detection of TA from **5t** would constitute good evidence for stepwise homolysis of even symmetrical azoalkanes; however, no such product was seen in our earlier thermal and photochemical studies of **5t** or even of **6t**.¹⁵ Since the BDE of methane (105.1 kcal mol⁻¹) is only slightly below that of cyclopropane, **6t** would be expected to behave like **1t**.



These considerations and our success in detecting TA's from **1t** led us to reinvestigate all of the previously studied dimethylallylazoalkanes^{12,15} plus two new ones. As shown in Table I, (a) the methyl compound **6** does give TA,¹⁶ (b) the amount of TA qualitatively decreases as one proceeds down the table, and (c) the yield of TA passes below our detection limit when R = *tert*-butyl.¹⁷ These results point to a more general role for diazenyl radicals than previously believed.

Two other experiments were carried out with **1t**. A degassed sample in hexadecane was heated for 17 h (one half-life) at 110 °C. HPLC analysis of the reaction mixture revealed that a small amount of **2t** had formed. It is therefore likely that both *cis* and *trans* isomers decompose via the same mechanism, though prior isomerization of **1t** to **1c** cannot be ruled out.⁶ In a second experiment, **1t** was irradiated at 366 nm in two solvents of widely different viscosity and quantum yields were determined by HPLC. As shown in Table II, disappearance of **1t** was less efficient, but more **2t** formed in hexadecane than in pentane. If TA arose from some kind of [1,3]-azo shift, one would not expect such a large

(14) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(15) Engel, P. S.; Bishop, D. J.; Page, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 7009.

(16) This revision of our earlier work¹⁵ is attributable to a much improved NMR spectrometer (Joel FX-90Q) and HPLC instrumentation (Beckman Model 342 with Model 165 detector).

(17) An authentic sample of the turnaround product from **10t** showed the N=NCMe₂ group as an NMR doublet at 4.47 ppm (C_6D_6).

(11) Porter, N. A.; Iloff, P. M. *Chem. Commun.* **1971**, 1575.

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

(13) In a private communication, Professor Porter indicated that he also observed **4c**.

Table III. Activation Free Energy for Stepwise Homolysis of $\text{RN}=\text{NCMe}_2\text{CH}=\text{CH}_2$

R	$\Delta G_{\text{obsd}}^{\ddagger}$ (298 °C) ^{a,b}	$\Delta G_{\text{D}}^{\ddagger,a,c}$	$k_{\text{D}}, \text{s}^{-1}$	τ, s^d
Ph	33.8 ^e	9.2	1.1×10^6	6.3×10^{-7} ^f
cyclopropyl	31.7	7.1	3.7×10^7	1.9×10^{-8}
Me	31.2	6.6	9.0×10^7	7.7×10^{-9}
<i>i</i> -Pr	29.4	4.8	1.9×10^9	3.7×10^{-10}
<i>t</i> -Bu	26.8	2.2	1.5×10^{11}	4.6×10^{-12}
dimethyl- allyl	24.6	0	6.2×10^{12}	1.6×10^{-13}

^a kcal mol⁻¹. ^b For thermolysis of *trans*-azoalkanes. See ref 12. ^c ($\Delta G_{\text{obsd}}^{\ddagger} - 24.6$) kcal mol⁻¹; see text. ^d Calculated lifetime of $\text{RN}=\text{N}\cdot$. ^e Estimated. ^f The lifetime of $\text{PhNN}\cdot$ has been estimated as 10^{-7} – 10^{-9} s,^{23a} $>10^{-8}$ s,³ and 3×10^{-7} s.^{23b}

viscosity effect. A treatment analogous to that of Pryor¹⁸ and Porter¹⁹ indicates that 12% of the diazenyl-alkyl pairs return to azoalkanes in pentane and 39% in hexadecane.²⁰

The above results can be rationalized in terms of the More O'Ferrall-Jencks-Thornton diagram²² shown in Figure 1. The starting azoalkane lies at the right, front corner while the ultimate products lie at the left, rear corner. The heavy line connecting these two points is the concerted, asynchronous pathway in which the weaker dimethylallyl-N bond is stretched to a greater degree at the transition state than is the stronger R-N bond. Since radical character in R \cdot is not well-developed at the transition state, this pathway explains why varying R has a smaller effect on the azoalkane thermolysis rate¹² than it has in the symmetrical compounds $\text{RN}=\text{NR}$. However, formation of TA requires that $\text{RN}=\text{N}\cdot$ recombine with dimethylallyl radical, indicating that in many cases, at least part of the reaction must proceed via the front, left corner. According to this view, making R \cdot a better radical allows the concerted, asynchronous pathway to compete better with the stepwise pathway; that is, $\Delta G_{\text{TS}}^{\ddagger}$ falls below $\Delta G_1 + \Delta G_{\text{D}}^{\ddagger}$. ($\Delta G_{\text{D}}^{\ddagger}$ is the activation free energy for loss of N_2 from $\text{RN}=\text{N}\cdot$.) $\Delta G_{\text{TS}}^{\ddagger}$ must represent the more favorable pathway for the case of R \cdot = *tert*-butyl since no turnaround azoalkane was seen from 10t.

Another interpretation of the results which is consistent with Neuman's important pressure study⁷ supposes that the concerted, asynchronous pathway is always of high energy⁶ and that the whole reaction proceeds via diazenyl radicals. Let us assume that $\Delta G_{\text{D}}^{\ddagger}$ is zero for $\text{H}_2\text{C}=\text{CHCMe}_2\text{N}=\text{N}\cdot$, that ΔG_1 is independent of R, and that a negligible barrier is required to re-form azoalkanes. The energy needed to reach the front, left corner in Figure 1 is

(18) Pryor, W. A.; Smith, K. J. *J. Am. Chem. Soc.* **1970**, *92*, 5403.

(19) Porter, N. A.; Landis, M. E.; Marnett, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 795.

(20) Though reasonable, these numbers are not to be taken too seriously because the low quantum yields in Table II suggest that photochemical re-isomerization of 1c competes with thermolysis. Light absorption by products 2t and 2c will also diminish the observed quantum yields. Furthermore, the treatment^{18,19} neglects β -scission of cyclopropyldiazenyl radical within the solvent cage, yet this process has recently been found to be important for phenyldiazenyl radicals.²¹ The re-isomerization problem was probably even more severe in Porter's study¹⁹ because his Φ 's were no more than 0.044 and the irradiation wavelength chosen corresponded to the λ_{max} of the *cis* isomer (3c).

(21) Neuman, R. C.; Lockyer, G. D. *J. Am. Chem. Soc.* **1983**, *105*, 3982.

(22) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; p 201.

(23) (a) Porter, N. A.; Marnett, L. J.; Lochmuller, C. H.; Closs, G. L.; Shobataki, M. *J. Am. Chem. Soc.* **1972**, *94*, 3664. (b) Brede, O.; Mehnert, R.; Naumann, W.; Becker, H. G. *O. Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 666.

(24) Yamashita, K.; Kaminoyama, M.; Yamabe, T.; Fukui, K. *Chem. Phys. Lett.* **1981**, *83*, 78.

therefore constant for all azoalkanes in Table I and is equal to the observed activation energy ($\Delta G_{\text{obsd}}^{\ddagger}$) for the symmetrical compound 5. When R is a poorer radical, $\Delta G_{\text{D}}^{\ddagger}$ increases, and the more persistent diazenyl radicals have a better chance of recombining with dimethylallyl within the solvent cage. $\Delta G_{\text{obsd}}^{\ddagger}$ for such an unsymmetrical azoalkane is then $\Delta G_1 + \Delta G_{\text{D}}^{\ddagger}$. Since we know both ΔG_1 and $\Delta G_{\text{obsd}}^{\ddagger}$ for thermolysis of several *trans* dimethylallyl azo compounds, the $\Delta G_{\text{D}}^{\ddagger}$ values in Table III are easily derived. Thermolysis of the *cis* isomers is influenced strongly by steric effects⁴ but would probably reveal the same substituent effect on $\Delta G_{\text{obsd}}^{\ddagger}$ in the absence of this complication. One can use our $\Delta G_{\text{D}}^{\ddagger}$'s to predict correctly which azo compounds will give TA. The rate constant for deazotization of diazenyl radicals (k_{D}) is first calculated from $\Delta G_{\text{D}}^{\ddagger}$ and the Eyring rate equation (cf. Table III). Since formation of TA requires that the dimethylallyl radical rotate before $\text{RN}=\text{N}\cdot$ loses N_2 , we then compare k_{D} with the rate of this rotation. The Stokes-Debye equation²⁵ for rotational diffusion gives a value of $k_{\text{rot}} = 3.4 \times 10^{10} \text{ s}^{-1}$ at 298 °C in benzene using an estimated radius of 2.5 Å for the dimethylallyl radical. Comparison with the k_{D} 's in Table III shows that rotation is faster than decomposition of *i*-PrN $=\text{N}\cdot$ but is slower than decomposition of *t*-BuN $=\text{N}\cdot$. This treatment predicts that TA will be seen from 8 but not 10, in accord with the results in Table I.

If the $\Delta G_{\text{D}}^{\ddagger}$ values in Table III were all about 7 kcal mol⁻¹ higher than shown, they would agree better with those calculated theoretically.^{6,24} One would then expect TA from all of the present azoalkanes unless the barrier to diazenyl-alkyl recombination were also higher than the 1–2 kcal mol⁻¹ associated with rotation of the dimethylallyl radical. Experimental support for higher barriers can be adduced from the appearance potential of CH_3^+ from azomethane (11.5 eV).²⁶ Using currently accepted heats of formation, we calculate that the first methyl-N bond dissociation energy is 38.6 kcal mol⁻¹. Since the overall activation energy for thermolysis of *trans*-azomethane is 52.3 kcal mol⁻¹,⁴ $\text{CH}_3\text{N}=\text{N}\cdot$ must surmount a barrier of 13.7 kcal mol⁻¹ to lose N_2 or to recombine with CH_3 . In accord with Dannenberg's calculation,⁶ the recombination barrier must generally be the lower one; otherwise, turnaround azoalkanes would not have been formed in the present work. Unfortunately, raising all $\Delta G_{\text{D}}^{\ddagger}$ values and diazenyl-allyl recombination barriers by 7 kcal mol⁻¹ predicts an unreasonably long lifetime^{3,23} for Ph-N $=\text{N}\cdot$.

In summary, the present results are consistent with a competition between mechanisms A and B or, better, with exclusive decomposition via (B) provided that the first step is reversible. On the basis of (B) and a few assumptions, we have shown that the calculated rate of nitrogen loss from $\text{RN}=\text{N}\cdot$ exceeds the rotation rate of dimethylallyl radical within the solvent cage when R is *tert*-butyl but not when it is isopropyl. Viscosity, scavenging, and product studies of the compounds described here should reveal how much diazenyl-dimethylallyl recombination occurs at the tertiary allylic site and the extent to which alkyldiazenyl radicals escape the solvent cage.

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Registry No. 1t, 87102-77-0; 3t, 41809-44-3; 5t, 57542-25-3; 6t, 57542-19-5; 7t, 87102-78-1; 8t, 57542-20-8; 9t, 87102-79-2; 10t, 57542-21-9.

(25) Debye, P. "Polar Molecules"; Dover Publications: New York, 1945; p 85.

(26) Gowenlock, B. G.; Majer, J. R.; Snelling, D. R. *Trans. Faraday Soc.* **1962**, *58*, 670.