Thermolysis of Cis and Trans Azoalkanes

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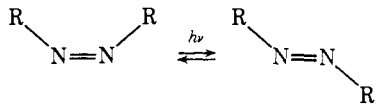
Abstract: Activation parameters for thermal decomposition of three new trans azoalkanes R—N=N—$C(CH_3)_2$—CH=CH_2 (R = CH_3, *i*-C_3H_7, and *t*-C_4H_9) are reported. The transition state for homolysis is characterized by different degrees of C–N bond stretching for the two incipient radicals, depending upon their stability. Thermolysis activation parameters have also been determined for four cis azoalkanes, including one cyclic compound. The ground state energy for cis azoalkanes is 7–8 kcal mol^{-1} higher than that for the trans isomers. Coupled with a steric effect, this energy difference explains the enormously greater lability of the cis azoalkanes.

Azoalkanes can exist in either the cis or trans configuration, but conversion of one form to the other can only be effected photochemically.[2] Virtually every acyclic azoalkane



prepared by normal synthetic procedures has been the trans isomer, with the exception of perfluoroazomethane.[4] Very recently, however, two chemical syntheses of cis–trans mixtures have appeared.[5,6] In the few compounds where both isomers are known, they differ drastically in physical properties, spectral properties, and stability toward extrusion of nitrogen.

The first cis azoalkane was reported by Hutton and Steel,[7] who isolated cis azomethane by irradiating the trans compound in solution. A few years later, Steel and coworkers[8] prepared *cis*-azoisopropane (*cis*-AIP), a compound which nicely illustrates the differences between the isomers (cf. Table I).

Although Table I shows that *cis*-AIP is much less stable thermally than trans, the difference is even greater when the α carbon is tertiary. Thus, Mill and Stringham[11] reported that the activation energy for thermolysis of *cis*-azo-*tert*-butane was about 20 kcal mol^{-1} less than that of trans; in fact, the cis was not isolable even at 0°. These authors made the important suggestion that photolysis of many trans azoalkanes in solution proceeds by photoisomerization to the labile cis isomers.

Because cis azoalkanes are a new class of compounds, studies of their decomposition are few indeed. The trans isomers, on the other hand, have been investigated for over 40 years, both in solution and in the gas phase.[12-22] Remarkably, the mechanism of their decomposition is still a point of controversy, some authors favoring concerted two-bond scission (eq 1) and others one-bond scission (eq 2). The

$$\text{R—N=N—R}' \longrightarrow \text{R}\cdot + \text{N}\equiv\text{N}\cdot\text{R}' \quad (1)$$

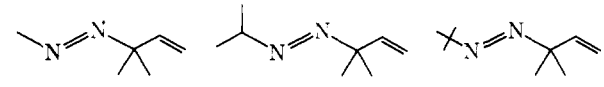
$$\text{R—N=N—R}' \longrightarrow \text{R—N=N}\cdot + \cdot\text{R}' \longrightarrow \text{R}\cdot + \text{N}\equiv\text{N}\cdot\text{R}' \quad (2)$$

principal question is whether the diazenyl radical (R—N=N·) is a discrete intermediate. When R is phenyl, the evidence is overwhelmingly in favor of one-bond scission. Porter's studies of phenylazoalkanes[23,24] deserve special mention, but such techniques as viscosity[13] and pressure dependence[25] of the rate have also provided evidence for one-bond cleavage in highly unsymmetrical azoalkanes. Seltzer's results using secondary deuterium isotope effects agree with the one-bond mechanism when R is phenyl but suggest increasing two bond character as the azoalkane becomes more symmetrical.[26]

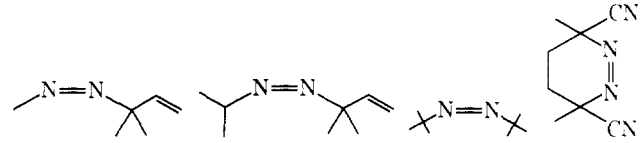
Although the intermediacy of phenyldiazenyl radicals in thermolysis of arylazoalkanes has been demonstrated, alkyldiazenyl radicals have proved far more elusive.[26-29] Part of the evidence that they exist at all derives from CIDNP studies of azoalkane photolysis but, to our knowledge, alkyldiazenyl radicals have not been implicated in azoalkane thermolysis by this technique.[24,27] However, Seltzer[17b] has shown by optical activity loss experiments that methyldiazenyl radicals are involved in thermolysis of (−)-methylazo-α-phenylethane.

Another method which has been used to decide between eq 1 and 2 is comparison of thermolysis rates of variously substituted azoalkanes.[16,18] Simply stated, two-bond scission predicts that the stability of both incipient radicals will influence the rate, whereas one-bond scission should occur preferentially to give the more stable radical, and therefore the rate should not depend on the nature of the less stable radical. The bulk of the evidence for solution studies favors eq 1, but certain gas phase pyrolyses[16] are consistent with eq 2.

In the present work, we have measured activation parameters for thermolysis of three trans azoalkanes (**1t–3t**) and four cis azoalkanes, (**1c, 2c, 4c, 5**) including one cyclic compound. Our data for the trans isomers are best accommodated by the two-bond scission mechanism with the proviso



1t **2t** **3t**



1c **2c** **4c** **5**

that the degree to which the second C–N bond breaks in the transition state depends upon the stability of the second R· radical.[18,20,26] After correction for steric effects, the cis azoalkanes are found to have a 7–8 kcal mol^{-1} lower free energy of activation for thermolysis than the trans compounds. This difference is ascribed to a higher energy ground state for the cis isomer.

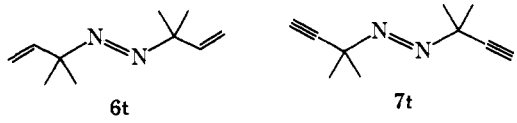
Synthesis of the Azoalkanes. Although several methods exist for the synthesis of symmetrical azoalkanes,[30] especially those with primary and secondary α carbons,[31] the unsymmetrical compounds **1t–3t** posed a real challenge. The best procedure proved to be a simple extension[32] of Ohme's sulfamide oxidation,[33] as illustrated below. While this work was in progress, Timberlake[34] prepared the sulfamyl chloride from *tert*-butyl alcohol plus chlorosulfonyl

$$R{-}NH_2 \xrightarrow{HCl} R{-}\overset{+}{N}H_3Cl^- \xrightarrow{SO_2Cl_2} R{-}NH{-}SO_2Cl \xrightarrow{R'{-}NH_2}$$
$$R{-}NH{-}SO_2{-}NH{-}R' \xrightarrow[NaOH]{NaOCl} R{-}N{=}N{-}R'$$

isocyanate[35] and used it to synthesize *tert*-butylazo-*tert*-octane. The relatively low yields of this method and the commercial unavailability of chlorosulfonyl isocyanate lead us to favor the Weiss-Schulze procedure.[32] The cis compounds **1c, 2c,** and **4c** were too unstable for isolation and were always prepared in situ by irradiation of the trans isomers. Compound **5,** which was also extremely unstable, was made in situ by *tert*-butyl hypochlorite oxidation of the known hydrazine.[36]

Results

Rates of decomposition for **1t–3t** were determined using an automated constant-volume kinetic apparatus[37] to follow nitrogen evolution. Table II shows the individual rate constants for these compounds and for **6t** and **7t,** while Table IV includes the activation parameters derived from a least-squares fit of the data. Arrhenius plots for the unsymmetrical azoalkanes, which are displayed in Figure 1, show good straight lines for **2t** and **3t;** however, close inspection of the data for **1t** in *p*-diisopropylbenzene reveals some curvature in the gas evolution points. To check whether the choice of solvent was related to this problem, three runs were carried out in diphenyl ether containing 0.26 *M* benzoquinone,[26] but the rates were close to the previous ones. A separate series of rate measurements was done using NMR to monitor the disappearance of azoalkane. Although the curvature is not apparent for these points (cf. Figure 1), the method depends on NMR integrals and is therefore less accurate than gas evolution data. Induced decomposition is probably not responsible for the curvature in the nitrogen evolution points, as will be discussed later. Since no satisfactory explanation comes to mind, we chose to use all available data (13 points) to calculate the activation parameters for **1t** shown in Table IV.



6t

7t

Thermolysis of cis azoalkanes **1c, 2c,** and **4c** was followed by nitrogen evolution in a manner similar to that used for the trans compounds, except that the bath temperature was at least 100° lower. The rate difference between the isomers is so large that thermolysis of trans does not contribute to the observed nitrogen evolution from cis. Because **5** had to be generated chemically, its disappearance was more conveniently monitored in a stirred cell in a Cary 17 uv-visible spectrometer. The cell was surrounded by a low-boiling liquid which refluxed from a Dry Ice condenser, thus maintaining a constant temperature in the region of 0°. The small temperature range employed is a consequence of the unavailability of suitable condensable gases.

The data for thermolysis of cis azoalkanes are summarized in Tables III and IV, and Arrhenius plots are shown in Figure 2. Activation parameters for **4c** and **5** have been reported previously,[11,39] and these are included in Table IV for comparison purposes.

Considerable effort was expended in an attempt to run kinetics on still more labile cis azoalkanes. Since neither of the previous methods was suitable at temperatures below −40°, a matrix isolation cryogenic apparatus was modified for the present purposes. The problem of keeping the azoalkanes in solution at low temperatures was solved by irradiating them in methyl methacrylate solution contained in a rectangular Teflon mold. A portion of the azoalkane decomposed, and the resulting free radicals polymerized the solvent, producing a clear plastic block. The block was cooled to about −150° and irradiated until part of the remaining azoalkane had been converted to the cis isomer. Since the uv band of cis always fell at longer wavelength than that of trans, the thermal disappearance of cis was readily monitored as a function of temperature. Figure 3 shows spectra of compound **6** at various times during such an experiment, while Table V lists approximate decomposition temperatures for eight cis azoalkanes.

Table I. Survey of the Properties of *cis*- and *trans*-Azoisopropane

	trans-AIP	*cis*-AIP
Bp[a]	88.5° (760 nm)	66° (77 nm)
Retention time[a,b]	1.0	1.6
Uv, λ_{max} (ϵ)[c]	359 (14.5)	382 (140)
NMR δ ppm[d]	1.19 (d, J = 6.5 Hz)	1.23 (d, J = 6.5 Hz)
	3.53 (septet)	3.98 (septet)
$\Delta H^{\pm}$[e]	47.3 ± 1.0[f]	39.9 ± 1.8[g]
$\Delta S^{\pm}$[e]	14.1[f]	18.9 ± 4.1[g]

[a] Reference 5. [b] Relative VPC retention time on a 6 ft 10% SF-96 column at 120°. [c] Reference 9. [d] Reference 8. [e] Activation enthalpy (kcal mol^{-1}) and entropy (eu) for thermal extrusion of nitrogen. [f] Reference 10. [g] C. Steel, private communication.

Table II. Rate Constants for Thermolysis of Trans Azoalkanes

Compd[a]	Temp, °C	$k \times 10^4$, sec^{-1}	Compd	Temp, °C	$k \times 10^4$ sec^{-1}
1t	114.55	1.02	3t	73.72	0.869
	119.16	1.65		77.00	1.24
	123.83	2.68		80.31	1.83
	128.51	4.66		83.70	2.64
	133.33	8.44		87.08	3.80
1t[b]	118.46	1.50	6t[d]	42.03	0.595
	123.53	2.62		46.87	1.22
	128.49	5.50		49.98	1.73
	133.53	9.58		53.80	2.69
	138.73	16.1		57.39	4.54
1t[c]	114.60	1.12	7t[d]	41.32	0.537
	123.83	2.63		44.76	0.832
	133.35	8.02		48.20	1.30
2t	97.41	1.15		52.90	2.44
	101.72	1.97		57.19	4.39
	106.06	3.19			
	110.62	5.56			
	115.06	9.22			

[a] 0.2 *M* in *p*-diisopropyl benzene followed by nitrogen evolution unless otherwise specified. [b] Followed by NMR. [c] 0.26 *M* benzoquinone in diphenyl ether as solvent. [d] In xylene.

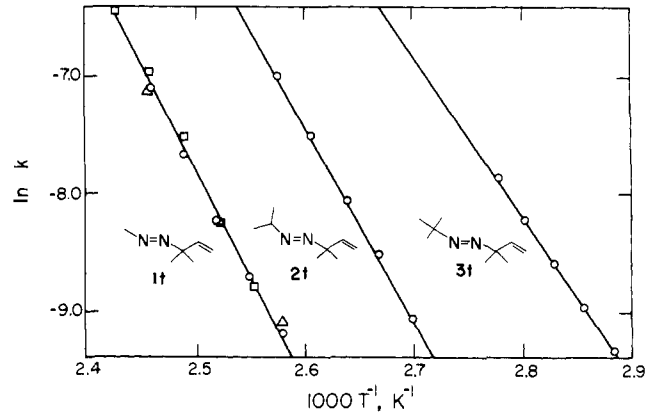


Figure 1. Arrhenius plot for trans azoalkanes. k is in sec^{-1}. (○) Gas evolution in *p*-diisopropylbenzene; (△) gas evolution in 0.26 *M* benzoquinone diphenyl ether; (□) NMR in *p*-diisopropylbenzene.

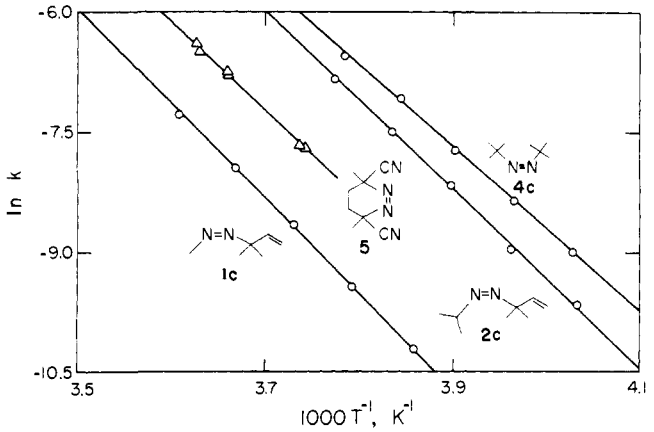


Figure 2. Arrhenius plot for cis azoalkanes. k is in sec^{-1}. (○) Gas evolution; see Table III for solvents. (△) Uv spectroscopy.

Table III. Rate Constants for Thermolysis of Cis Azoalkanes

Compd	Temp, °C	$k \times 10^4$, sec^{-1}	Compd	Temp, °C	$k \times 10^4$, sec^{-1}
1c[a]	−13.89	0.362	4c[b]	−24.82	1.22
	−9.38	0.777		−20.93	2.31
	−5.04	1.70		−17.02	4.39
	−0.54	3.50		−13.00	8.50
	+4.00	6.82		−8.95	14.3
2c[a]	−25.09	0.630	5[c]	−6.06	4.60
	−20.83	1.26		−5.60	4.68
	−16.65	2.87		+0.03	11.4
	−12.43	5.58		+0.06	11.7
	−8.20	11.0		+2.41	15.2
				2.52	16.4

[a] In acetone. [b] In ethanol containing triethylamine (2 drops/7 ml). [c] In dichloromethane.

Table IV. Activation Parameters[a] for Thermolysis of Azoalkanes

Compd	$\Delta H^{\ddagger}$, Kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$ (298°), kcal mol^{-1}	Reference
1t	35.3 ± 1.0	13.6 ± 2.5	31.2 ± 1.2	This work
1c	23.1 ± 0.3	10.5 ± 1.1	20.0 ± 0.4	This work
2t	32.9 ± 0.3	11.8 ± 0.8	29.4 ± 0.4	This work
2c	21.8 ± 0.4	10.5 ± 1.6	18.7 ± 0.6	This work
3t	26.8 ± 0.2	−0.1 ± 0.6	26.8 ± 0.3	This work
4t	42.2 ± 0.3	16 2 ± 0.6	37.4 ± 0.3	38
4c	19.9 ± 0.4	4.3 ± 1.5	18.7 ± 0.6	This work
4c	22.5 ± 2.0	11.0 ± 2.3	19.2 ± 2.1	11
5	21.2 ± 0.6	5.9 ± 2.3	19.5 ± 0.9	This work
5	17.1	−8.7	19.7	39
AIBN[b]	30.1 ± 0.4	7.9 ± 1.3	27.7 ± 0.6	40
6t	26.1 ± 0.8	5.0 ± 2.5	24.6 ± 1.1	This work'
7t	26.7 ± 0.5	6.7 ± 1.4	24.7 ± 0.6	This work

[a] Tolerances are the standard deviation from the mean. [b] Azoisobutyronitrile.

Seeking to refine these crude measurements, we constructed a new cryogenic apparatus which would hold a constant temperature within 0.01° over the range −170 to 0°. Our intention was to determine the decomposition rate at a series of fixed temperatures and then calculate activation parameters. Unfortunately, irradiation of the cold samples did not always produce cis, probably on account of variations in the viscosity of the polymer. Furthermore, equilibration times were long, and often the cis isomer had disappeared by the time the sample had reached a constant temperature. Even though these experiments were unsuccessful, the data of Table V provide a rough idea of the stability of various cis azoalkanes. Moreover, every trans azoalkane which we irradiated eventually gave some cis isomer, if the temperature was sufficiently low.

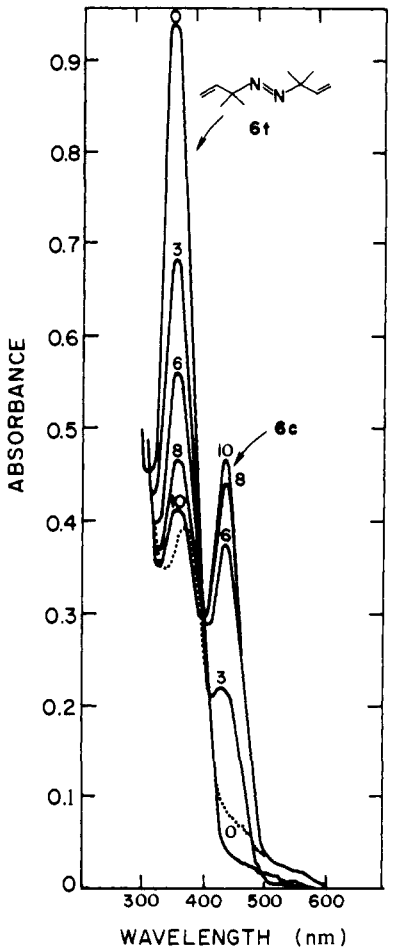


Figure 3. Photolysis of 6t in polymethyl methacrylate at 366 nm and −150°. The numbers above the solid curves are the irradiation time in minutes, while the dotted curve was obtained after warming to 25°.

Discussion

Comparison of Cis and Trans Azoalkanes. It is apparent from Tables IV and V that cis azoalkanes decompose enormously faster than their trans isomers. A quantitative comparison is made in Table VI, based on the data obtained in this laboratory wherever a choice exists. The previously reported[11,39] activation parameters for **4c** and **5** were derived from only two kinetic points as opposed to our five to six points; moreover, the negative activation entropy for **5** is extremely unlikely for thermolysis of an azo compound. As is often true, however, the differences in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for these two compounds nearly cancel in calculating $\Delta G^{\ddagger}$.

Since $\Delta G^{\ddagger}$ is most reliable in the region where the rate measurements were made, a problem arises as to how to best compare $\Delta G^{\ddagger}$'s for the cis and trans isomers, whose rates were determined in very different temperature ranges. We have chosen to calculate all $\Delta G^{\ddagger}$'s at 298° regardless of the temperature of the kinetic runs. However, it can be shown that the difference in $\Delta G^{\ddagger}$ between two compounds does not depend strongly on the temperature of comparison (cf. eq 3).

$$\Delta\Delta G^{\ddagger} \equiv (\Delta G_{cis}{}^{T_1} - \Delta G_{trans}{}^{T_1}) - (\Delta G_{cis}{}^{T_2} - \Delta G_{trans}{}^{T_2}) = (T_2 - T_1)(\Delta S_{cis}{}^{\ddagger} - \Delta S_{trans}{}^{\ddagger}) \quad (3)$$

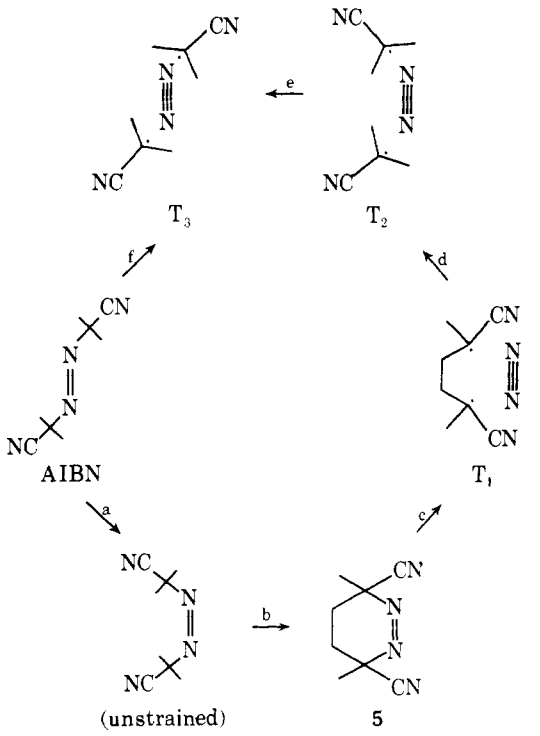
Table VI lists the mid-range temperature for kinetic studies on each compound and the uncertainty in $\Delta\Delta G^{\ddagger}$ caused by making the comparison at one or the other extreme temperature, as calculated from eq 3. Except for azo-*tert*-butane,

Table V. Wavelength Maxima and Decomposition Temperatures for Cis Azoalkanes in Polymethyl Methacrylate

Compd	λ_{max}(trans), nm	λ_{max}(cis), nm	Temp, °C[a]
6	366	442	−120
7	350	420	−110
3	366	444	−110
Azocumene	360	434	−100
Azo-*tert*-octane	364	444	−70
AIBN	341	390	−60
2	364	385	−30
1	363	380	−20

[a] The half-life of cis azoalkane was on the order of 10 min at these temperatures.

Scheme I. Thermochemical Cycle for a Six-Membered Azoalkane



the variation in $\Delta\Delta G^{\ddagger}$ due to temperature is less than the standard deviation.

The difference in free energy of activation between cis and trans ($\Delta\Delta G^{\ddagger}$) is seen to vary from one compound to another; however, these figures are undoubtedly influenced by a steric strain factor. An estimate of this effect can be obtained by comparing azoalkanes with olefins,[11] for which thermodynamic data are available.[41] Admittedly, the bond lengths and angles differ for these two species,[4,42] but the analogy nevertheless leads to a reasonably consistent set of numbers. We shall assume that the entropy difference between cis and trans olefins is negligible and therefore that the free energy difference ($\Delta\Delta G_f$) is equal to the known enthalpy difference.[43] Thus, since *cis*-di-*tert*-butylethylene is 10.5 kcal mol^{-1} less stable than trans,[41] *cis*-azo-*tert*-butane (**4c**) is taken to possess 10.5 kcal mol^{-1} of steric strain. Subtracting this figure from the observed $\Delta\Delta G^{\ddagger}$ of 18.7 and trans azoalkane of 8.2 kcal mol^{-1}. Applying the same reasoning to **1** and **2**, we deduce two other values for this inherent difference of 7.3 and 6.8 kcal mol^{-1}. Support for the tacit assumption that the isopropyl group takes up a conformation with no more strain than methyl will be given below.

The case of **5** vs. AIBN is considerably more complex, as shown in Scheme I. The letters a–f designate real and hypothetical reactions, while T_{1-3} are the transition states (taken to be the radicals) for loss of nitrogen from **5**, from *cis*-AIBN, and from *trans*-AIBN, respectively. Since ΔG_c and ΔG_f are known to be 19.5 and 27.7 kcal mol^{-1}, we can write $\Delta G_a + \Delta G_b + \Delta G_d + \Delta G_e = 8.2$ kcal mol^{-1}. Assuming that $\Delta G_b = -\Delta G_d$, we find that the inherent difference between a cis and a trans azoalkane, $\Delta G_a + \Delta G_e$, comes out 8.2 kcal mol,$^{-1}$ in remarkable agreement with the estimates from acyclic azoalkanes. However, this agreement may be partly fortuitous because b and −d are not strictly comparable. Thus b should possess a lower ΔG than does the reverse of d on account of the expected larger ΔS for cyclization. On the other hand, any ring strain in **5** will tend to raise ΔG_b. These two effects appear to be roughly equal.

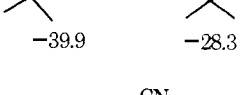
Table VI. Comparison of Cis and Trans Azoalkanes[a]

Compd	$\Delta G^{\ddagger}$ (298°)	$\Delta\Delta G^{\ddagger}$ (298°)[b]	T_{mid}[c]	$\Delta\Delta\Delta G^{\ddagger}$[d]	$\Delta\Delta G_f$[e]	$\Delta\Delta G^{\ddagger} - \Delta\Delta G_f$
1t	31.2		128			
		11.2 ± 1.3		0.41	3.9	7.3
1c	20.0		−5			
2t	29.4		106			
		10.7 ± 0.7		0.16	3.9	6.8
2c	18.7		−17			
4t	37.4		183			
		18.7 ± 0.7		2.40	10.5	8.2
4c	18.7		−17			
5	19.5		−2			
		8.2 ± 1.1		0.11	0	8.2
AIBN	27.7		55			

[a] All entries in kcal mol^{-1}, except for T_{mid}. [b] $\Delta G^{\ddagger}$ (trans) − $\Delta G^{\ddagger}$ (cis). [c] Middle of temperature range used for rate studies, °C. [d] See eq 3. [e] Estimated steric difference between cis and trans; see text.

We conclude from Table VI that cis azoalkanes inherently decompose with a 7–8 kcal mol^{-1} lower $\Delta G^{\ddagger}$ than trans azoalkanes, in good agreement with the data for AIP (Table I). The next logical question is whether this difference is due to a higher energy ground state for cis vs. trans, or whether it is a transition state effect. Neither explanation runs contrary to intuition, but the meager experimental facts hint that the former is more important. In particular, a survey of the literature reveals many instances where cis or cyclic azoalkanes were purified only with great difficulty, on account of their facile tautomerization to hydrazone.[5,7,44-49] Trans azoalkanes, on the other hand, are readily purified and are stable to storage. These observations are consistent with, but of course do not demand, a higher energy ground state for the cis azo linkage.

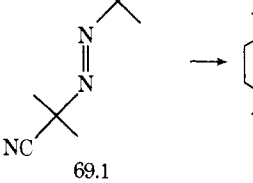
A more convincing argument involves another comparison of azoalkanes with olefins, as shown in the two hypothetical reactions below. ΔH_f for the olefins and AIBN was calculated from group values,[19,50] while ΔH_f for **5** was estimated from combustion data on 1,2-diaza-3,3,6,6-tetramethylcyclohexene.[51] The difference between the two reac-



$\Delta H_r = 11.6$ kcal mol^{-1} (4)

−39.9 −28.3

$\Delta H_f =$



$\Delta H_r = 18.6$ kcal mol^{-1} (5)

69.1 87.7

tion heats (7.0 kcal mol^{-1}) represents the additional enthalpy required to bring the azo group into the cis configuration. Making the reasonable assumption that reactions 4 and 5 have the same value of ΔS, we see that this 7.0 kcal

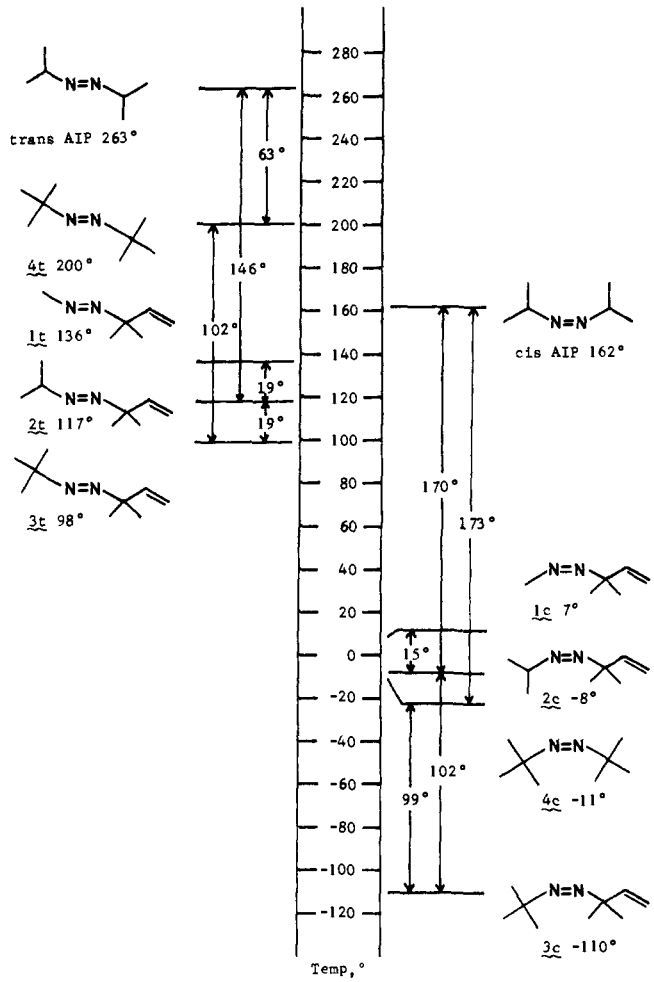


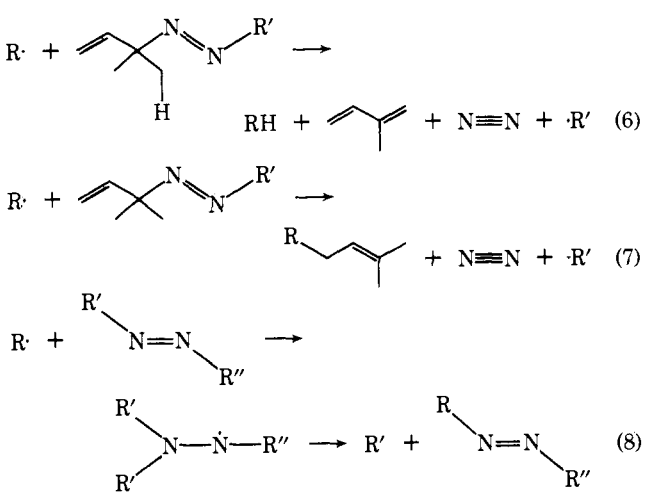
Figure 4. Azoalkane decomposition temperatures corresponding to a half-life of 10 min. Temperature differences discussed in the text are indicated by arrows.

mol^{-1} free energy difference is in good agreement with that obtained from the kinetic studies. This suggests that the difference in $\Delta G^{\ddagger}$ between cis and trans azoalkanes is a ground state effect. The reason for the extreme lability of many acyclic cis azoalkanes (cf. Table V) is steric strain caused by placing bulky groups on the same side of the azo linkage. Thus, *cis*-AIBN decomposes far more readily than **5**.

Figure 4 illustrates the magnitude of this steric effect and serves as a vehicle for other interesting comparisons. Instead of using conventional rate enhancement factors, we have tabulated temperatures at which the thermolysis half-life is 10 min. This representation avoids the very large extrapolations which would be required in the other method and allows us to include **3c,** for which activation parameters are unknown. The 63° difference between **4t** and *trans*-AIP is purely a radical stability effect, but the 173° difference in the cis isomers must be largely of steric origin. Similarly, **3t** is 19° less stable than **2t,** but the difference is 102° in the cis isomers. It is also apparent from Figure 4 that the stability difference between **1t** and **2t** is nearly the same as that between **1c** and **2c,** supporting our earlier assumption that the steric strain due to isopropyl is about the same as that of methyl. Comparison of **3t** and **4t** on the one hand with **3c** and **4c** on the other, suggests equal steric effects of methyl and vinyl groups; moreover, the effect of a radical stabilizing group on the cis isomer is the same as on the trans. A similar trend is seen in *trans*-AIP and **2t** vs. *cis*-AIP and **2c.** The larger temperature gap (170°) in the cis compounds compared with trans (146°) shows a considerable steric effect of juxtaposed dimethylallyl and isopropyl groups.

The Mechanism of Azoalkane Thermolysis. We approach the question of one- vs. two-bond cleavage by presenting activation parameters for some symmetrical and unsymmetrical azoalkanes in Table VII. The columns headed $\Delta\Delta G^{\ddagger}$ are the differences between the unsymmetrical azoalkane and its related more stable and less stable symmetrical azoalkanes. For example, $\Delta\Delta G^{\ddagger}$ between azomethane and methylazoisopropane is 3.5 kcal mol^{-1}, while $\Delta\Delta G^{\ddagger}$ between methylazoisopropane and azoisopropane is 0.7 kcal mol^{-1}. If the one-bond mechanism were valid, $\Delta\Delta G_2^{\ddagger}$ would be zero because the nature of the second incipient radical should be unimportant. Out of 13 comparisons, only the compounds studied by Crawford and coworkers[16] behave in this manner; in fact, their work includes the only negative $\Delta\Delta G^{\ddagger}$. In most other cases, $\Delta\Delta G_2^{\ddagger}$ is greater than zero, but less than $\Delta\Delta G_1^{\ddagger}$,[62] suggesting that some breaking of the second R–N bond must occur during thermolysis of azoalkanes. Since Crawford's rate measurements were carried out in the gas phase and most of the others were done in solution, it is possible that the mechanism is different in the two phases. When the activation energy for symmetrical azoalkanes is plotted vs. the R–H bond dissociation energy, a linear[37] Polanyi plot[55] is obtained. However, this plot for symmetrical azoalkanes alone is insufficient to distinguish one-bond from two-bond scission, as already discussed by Crawford.[16] The required experiment consists of measuring activation parameters for a set of unsymmetrical azoalkanes in both phases; however, no such study has been reported.

The possibility that much of the solution work is in error because of bimolecular reactions of azoalkanes is worthy of brief consideration. Two mechanisms for induced decomposition of the compounds examined here are shown in eq 6 and 7, while radical attack on the azo linkage is illustrated



in eq 8. All of these undesired reactions depend on the liberation of free radicals, which is highly unlikely in the solvents employed in this study. A methyl radical from decomposition of **1t,** for example, should react instantly with *p*-diisopropylbenzene. In the case of **6t,** it might be argued that the dimethylallyl radical will be sufficiently long-lived to enter into reactions 6–8, but we have shown in this case that the decomposition rate constant is unaffected by addition of the powerful free radical scavengers 2,2,6,6-tetramethylpiperidine-1-oxyl and Koelsch radical. Moreover, the kinetic plots for all compounds were always excellent straight lines to at least 3 half-lives. We conclude that the present solution studies, and probably most others, are not complicated by bimolecular reactions.

Table VII. Selected Activation Parameters (kcal mol^{-1}) For Azoalkanes R—N=N—R'

R	R'	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$ (298°)	$\Delta\Delta G_1^{\ddagger}$	$\Delta\Delta G_2^{\ddagger}$	Ref
Me	Me	51.3	13.8	47.2			52
n-Pr	*n*-Pr	44.6	5.0	43.1			53
i-Pr	*i*-Pr	47.3	14.1	43.1			10
t-Bu	*t*-Bu	42.2	16.2	37.4			38
Benzyl	Benzyl	34.3	5.6	32.7			54
Allyl	Allyl	35.2	9.9	32.3			55
α-Phen[a]	α-Phen[a]	31.8	6.7	29.8			56
2-Cyano[b]	2-Cyano	30.1	7.9	27.7			40
Cumyl	Cumyl	29.0	11.0	25.7			57
α,α-DiMe[c]	α,α-DiMe[c]	26.1	5.0	24.6			58
Me	*i*-Pr	46.4	8.9	43.8	3.5	0.7	59
Me	α-Phen[a]	37.7	14.0	33.6	13.7	3.8	27
i-Pr	α-Phen[a]	35.6	9.3	32.9	10.2	3.1	56
i-Pr	Cumyl	35.9	14.0	31.7	11.4	6.0	56
t-Bu	Cumyl	31.5	8.5	29.0	8.4	3.3	60
Me	Allyl	34.7	4.6	33.3	14.0	1.0	16
n-Pr	Allyl	34.8	6.7	32.8	10.3	0.5	16
t-Bu	Allyl	29.1	−2.7	29.9	7.5	−2.4	16
Me	α,α-DiMe[c]	35.3	13.6	31.2	16.1	6.6	This work
i-Pr	α,α-DiMe[c]	32.9	11.8	29.4	13.7	4.8	This work
t-Bu	α,α-DiMe[c]	26.8	−0.1	26.8	10.5	2.2	This work
t-Bu	2-Cyano[b]	34.2	15.0	29.7	7.7	2.0	61
Benzyl	α-Phen[a]	35.6	12.1	32.0	0.7	2.2	46

[a] α-Phenylethyl. [b] 2-Cyanopropyl. [c] α,α-Dimethylallyl.

Interestingly, reaction 8 has been shown[16] to occur during gas phase decomposition of allylazomethane, although it had virtually no effect on the activation parameters. For thermodynamic reasons, this reaction must proceed such that a less stable radical displaces a more stable radical. Since the resulting symmetrical azoalkane is likely to be stable at the temperature at which the unsymmetrical one was studied, it should not contribute to the observed rate constant, but it should build up to chemically detectable levels. However, we have never observed formation of azomethane during sealed NMR tube decomposition of **1t.**

Other evidence for one-bond cleavage of azoalkanes has been presented. In a clever analysis, Benson[19] has shown that the activation parameters for many azoalkanes can be predicted by assuming one-bond cleavage and fitting the kinetics to the thermodynamics of this process. In fact, we have used his reasoning with new thermochemical data[50] to deduce a revised group value for diazenyl (-N=N·) of 60.2 kcal mol^{-1}. However, Benson also pointed out that this good agreement between prediction and observation does not demand the one-bond mechanism so that even the revised diazenyl group value is speculative. Independent support for one-bond scission was derived primarily from the following argument, involving the energy of the second π bond in nitrogen (E_π).

E_a for azomethane decomposition should equal D_1 if the one-bond mechanism is correct, but E_a will fall below D_1 as two-bond character increases because some energy is recovered as the second π bond of nitrogen forms.

$$CH_3{-}N{=}N{-}CH_3 \longrightarrow CH_3{-}N{=}N\cdot + \cdot CH_3 \quad D_1 \quad (9a)$$

$$CH_3{-}N{=}N\cdot \longrightarrow CH_3\cdot + N{\equiv}N \quad D_2 \quad (9b)$$

The sum of reactions 9a and 9b is the complete decomposition of azomethane to two methyl radicals plus nitrogen, for which we can write

$$D_1 + D_2 = 2\Delta H_f(\cdot CH_3) - \Delta H_f(CH_3{-}N{=}N{-}CH_3) = 68.0\text{-}43.8 = 24.2 \text{ kcal mol}^{-1}$$

In this calculation, Benson used a value for ΔH_f of azomethane derived from Coates and Sutton's early combustion work on azoisopropane.[63] Since E_a = 52.5 kcal mol^{-1}, he concluded that $D_1 \geq 52.5$ kcal mol^{-1}, $D_2 \leq -28.3$ kcal mol^{-1} and $E_\pi \sim D_1 - D_2 \geq 80.8$ kcal mol^{-1}. This figure for E_π, which was already unexpectedly high, would become still larger if two bond cleavage occurred. Hence, the two-bond mechanism was considered unlikely. We now know[50] that $\Delta H_f(CH_3{-}N{=}N{-}CH_3)$ is about 32.1 kcal mol^{-1} instead of 43.8 kcal mol^{-1} which leads to E_π = 69.1 kcal mol^{-1}. Since this new value is actually below the π-bond energy of carbonyls and alkenes, there is room for some breaking of the second C-N bond in the transition state.

In the present series of compounds, **1t, 2t, 3t, 6t,** the activation parameters clearly depend upon the nature of the less stable radical when the more stable radical is held constant (cf. Table IV). A monotonic decrease in $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ attends an increase in the stability of the less stable radical. This result is consistent with the picture presented by others[18,20,26] in which the transition state for azoalkane thermolysis is characterized by breaking of both C-N bonds, but not necessarily to the same degree. The asymmetry of the transition state reflects the stability difference of the incipient radicals. It is not clear why the mechanism should be fundamentally different in the gas phase than it is in solution but rate measurements for the same set of unsymmetrical azoalkanes in both phases will be required to reach a final decision on this point.

A referee has pointed out that the kinetic method can only tell how unequal bond breaking is at the transition state but not what happens afterward. Given that azoalkane thermolysis proceeds by stretching of both C-N bonds, it is conceivable that, at some point on the energy surface after the transition state, the stronger C-N bond begins contracting while the weaker one breaks completely. The resulting diazenyl radical would later lose nitrogen. Although this sequence may describe the situation in phenylazoalkanes, we consider it less and less likely in the series **1t, 2t, 3t, 6t,** because the second C-N bond is stretched at the transition state to a greater extent in this order. It seems reasonable that the bonds which are stretched in the transition state will be broken in the products, particularly since decomposition of alkyldiazenyl radicals is calculated to be exothermic. It is nevertheless true that the kinetic method alone would not reveal a potential minimum for diazenyl radical; consequently, efforts to detect this species by other means are currently under way.

Experimental Section

General. Melting points were determined in capillary tubes on a Mel-Temp apparatus and are uncorrected. Proton magnetic resonance spectra (CCl_4 solvent unless otherwise specified) were obtained on Varian A56/60-A and Perkin-Elmer R-12 spectrometers. Infrared spectra were recorded on a Beckman IR-8 and ultraviolet-visible spectra on Cary 14 and 17 spectrometers. Mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-110 high resolution mass spectrometer. Elemental analyses were done by Elek Microanalytical Labs of Torrance, Calif.

Synthesis of Azoalkanes. 2-Amino-2-methyl-3-butyne was prepared from 2-chloro-2-methyl-3-butyne by reaction with $NaNH_2$ in NH_3, as described by Hennion and Teach.[64] In the later stages of this work, the amine became available from Aldrich Chemical Co., Inc. It was purified by drying over KOH and then distilling from KOH: bp 76°, mp 20° (lit.,[64] bp 79–80°, mp 18°); NMR δ 1.33 (s, 6 H), 1.58 (s, 2 H), 2.20 (s, 1 H).

2-Amino-2-methyl-3-butene. A solution of 25 g (0.3 mol) of 2-amino-2-methyl-3-butyne in 100 ml of pentane was placed in a pressure bottle, and 100 mg each of powdered KOH and 5% Pd/$BaCO_3$ was added. The theoretical amount of H_2 was taken up in 30 min on the Parr hydrogenator, using 40 psi initial H_2 pressure. The mixture was filtered through Celite and distilled through a 35-cm glass helix-packed column. Collection of the amine was begun at 68°, but the major fraction distilled at 72–73° (lit.[65] 74–76°), yield 18.8 g (73%): NMR δ 0.99 (s, 2 H), 1.15 (s, 6 H), 4.95 (m, 2 H), 5.95 (m, 1 H).

***N,N'*-Bis(1,1-dimethylpropargyl)sulfonimide.** A 500-ml flask was equipped with mechanical stirrer, thermometer, and Claisen adapter with 50-ml addition funnel and N_2 inlet. A solution of 20.0 g (0.24 mol) of 2-amino-2-methyl-3-butyne and 24.3 g (0.24 mol) of triethylamine in 75 ml of pentane was placed in the flask under N_2 and cooled to ca. −20° with a Dry Ice–acetone bath. A solution of 16.2 g (0.12 mol) of sulfuryl chloride in 25 ml of pentane was added dropwise over 3 hr, while the contents of the flask were vigorously stirred. The resulting white suspension was stirred for an additional hour at −20° and for 2 hr at 25°. After addition of 50 ml of water, the mixture was extracted with 4 × 100 ml ether, which was washed with 2 × 100 ml of water and 50 ml of NaCl solution. Evaporation of the ether gave 5.2 g of tan crystals. The basic water layer was acidified with 6 ml of glacial acetic acid and extracted with 8 × 100 ml of ether. The ether was washed with water, dried with $MgSO_4$, and evaporated to give 15.2 g of white crystals. Recrystallization of the combined products from ethyl acetate–hexane gave 19.5 g (75%) of white crystals, mp 121.8–123.4°: NMR ($CDCl_3$) δ 1.63 (s, 12 H), 2.53 (s, 2 H), 5.05 (s, 2 H); ir ($CHCl_3$) 1349, 1149 cm^{-1}. Anal. Calcd for $C_{10}H_{16}N_2O_2S$: C, 52.61; H, 7.06. Found: C, 52.27; H, 7.24.

***N,N'*-Bis(1,1-dimethylallyl)sulfonimide.** A solution of 6.0 g of *N,N'*-bis(1,1-dimethylpropargyl)sulfonimide in 100 ml of methanol was hydrogenated over 120 mg of 5% Pd/$BaSO_4$ and 250 mg quinoline on the Parr hydrogenator. H_2 uptake was complete in 12 min and, after filtration of the catalyst and evaporation of the solvent, the crude product was recrystallized from ethyl acetate–hexane, yield 5.5 g (90%): mp 85.7–88.0°; NMR ($CDCl_3$) δ 1.42 (s, 12 H), 4.43 (br s, 2 H), 5.12 (m, 4 H), 6.05 (m, 2 H); ir ($CHCl_3$) 1321, 1133 cm^{-1}. Anal. Calcd for $C_{10}H_{20}N_2O_2S$: C, 51.70; H, 8.68. Found: C, 51.45; H, 8.66.

Methyl sulfamyl chloride was prepared according to Weiss and Schulze:[32] bp 73–78° (0.1 mm) [lit.[32] bp 67° (0.03 mm)]; NMR δ 2.95 (d, J = 5, 3 H), 5.97 (br s, 1 H).

Isopropyl sulfamyl chloride was also prepared by the Weiss–Schulze procedure:[32] bp 54–60° (0.015 mm) [lit.[32] bp 70° (0.07 mm)]; NMR δ 1.35 (d, J = 7, 6 H), 3.90 (m, J = 7, 1 H), 6.16 (br d, J = 7, 1 H).

***tert*-Butyl Sulfamyl Chloride.** This compound was synthesized with considerably more difficulty than the two sulfamyl chlorides above; in fact, on some occasions, most of the *tert*-butylamine hydrochloride was recovered. Despite considerable experimentation, we have not yet discovered the reason for this variability.

To a suspension of 21.8 g (0.2 mol) of *tert*-butylamine hydrochloride in 100 ml of acetonitrile were added 54 g (0.4 mol) of SO_2Cl_2 and 20 drops of $SbCl_5$. After 7 hr reflux, like amounts of SO_2Cl_2 and $SbCl_5$ were added, and half these amounts were added again after 30 hr. Most of the hydrochloride had reacted after 100 hr; filtration gave back 15% of the starting amount. The resulting clear yellow solution was cooled and the reaction flask attached, via two −78° traps, a −196° trap, and a tube filled with KOH pellets, to a vacuum pump. The solvent and excess SO_2Cl_2 were removed at 25°. The residue was distilled, using tap water instead of ice–water in the condenser to prevent freezing of the product: yield 20.0 g (69%, based on consumed hydrochloride); bp 66–70° (0.015 mm); mp 23.5°; NMR ($CDCl_3$) δ 1.48 (s, 9 H), 6.18 (br s, 1 H).

***N-R-N'*-(1,1-dimethylpropargyl)sulfonimides (R = CH_3, *i*-C_3H_7, *t*-C_4H_9).** A 500-ml flask was equipped as for the preparation of *N,N'*-bis(1,1-dimethylpropargyl)sulfonimide, then charged with 0.1 mol each of 2-amino-2-methyl-3-butyne and triethylamine and 100 ml of dry ether. After cooling to −40° using a Dry Ice–acetone bath, a solution of the appropriate sulfamyl chloride (98 mmol) in 40 ml of ether was added dropwise with vigorous stirring. The reaction mixture was stirred cold for 30 min more and then was warmed to 25° using a water bath. Sufficient water to dissolve the triethylamine hydrochloride was added, and then the ether layer was separated, washed with 2 × 25 ml of water and 25 ml of NaCl solution, and dried over Na_2SO_4. Removal of the solvent and recrystallization from pentane–ether gave the crystalline sulfonimide. Yields were usually 55–75%. Melting points were R = CH_3, 82.0–84.2°; *i*-C_3H_7, 71.7–73.7°; *t*-C_4H_9, 113.6–115.1°. NMR ($CDCl_3$): R = CH_3, δ 1.62 (s, 6 H), 2.47 (s, 1 H), 2.72 (s, 3 H), 4.87 (br s, 2 H); *i*-C_3H_7, δ 1.25 (d, J = 6, 6 H), 1.63 (s, 6 H), 2.45 (s, 1 H), 3.60 (m, 1 H), 4.75 (br, 2 H); *t*-C_4H_9, δ 1.38 (s, 9 H), 1.62 (s, 6 H), 2.43 (s, 1 H), 4.60 (br, 2 H).

***N-R-N'*-(1,1-Dimethylallyl)sulfonimides (R = CH_3, *i*-C_3H_7, *t*-C_4H_9).** A solution of 7–10 g of the appropriate propargylsulfonimide in 50 ml of methanol was hydrogenated over 150 mg of 5% Pd/$BaSO_4$ and 300 mg of quinoline. At 40 psi, 1 equiv of H_2 was generally taken up in less than 30 min. Work-up with recrystallization from pentane–ether gave yields of 90–98%. R = CH_3: mp 66.3–69.0°; NMR ($CDCl_3$) δ 1.40 (s, 6 H), 2.62 (br s or d, J = 6, 3 H), 4.67 (br, 2 H), 5.07 (m, 2 H), 5.90 (m, 1 H); ir ($CHCl_3$) 1324, 1135 cm^{-1}. Exact mass of $M\cdot^+$ (calcd for $C_6H_{14}N_2O_2S$, 178.0775) 178.0774. R = *i*-C_3H_7: mp 66.9–68.2°; NMR ($CDCl_3$) δ 1.27 (d, J = 7, 6 H), 1.40 (s, 6 H), 3.59 (m, J = 7, 1 H), 4.55 (br, 2 H), 5.08 (m, 2 H), 6.03 (m, 1 H); ir ($CHCl_3$) 1330, 1130 cm^{-1}, exact mass of $M\cdot^+$ (calcd for $C_8H_{18}N_2O_2S$, 206.1088) 206.1088. R = *t*-C_4H_9: mp 110.5–112.5°; NMR ($CDCl_3$) δ 1.37 (s, 9 H), 1.45 (s, 6 H), 4.38 (br s, 1 H), 4.50 (br s, 1 H), 5.13 (m, 2 H), 6.07 (m, 1 H); ir ($CHCl_3$) 1318, 1132 cm^{-1}, exact mass of $M\cdot^+$ (calcd for $C_9H_{20}N_2O_2S$, 220.1245) 220.1243.

Azobis(1,1-dimethyl-2-propene) (6t). The hypochlorite oxidation procedure of Stowell[66] was employed with *N,N'*-bis(1,1-dimethylallyl)sulfonimide, except that the reaction mixture was allowed to stir at 0° overnight. Evaporation of the solvent at 0° and bulb-to-bulb distillation at 25° under reduced pressure gave the azo compound as a pale yellow oil: yield 1.4 g (79%); NMR δ 1.22 (s, 12 H), 5.02 (m, 4 H), 5.98 (m, 2 H); uv (hexane) λ_{max} 366 nm (ϵ 29.6).

Azobis(1,1-dimethyl-2-propyne) (7t). The Stowell procedure[66] was followed using *N,N'*-bis(1,1-dimethylpropargyl)sulfonimide and omitting the pentane. After stirring overnight at 0°, the solution was a pale pink and contained many crystals. The ground surfaces of the stirring shaft and the stoppers exposed to the inside of the flask had turned red. The solid azo was isolated by filtration at 0°. Although the color could be removed by sublimation, the solid still turned pink on storage, a phenomenon which is not understood: yield 2.75 g (59%); mp 24.5–26.0°; NMR δ 1.46 (s, 12 H), 2.43 (s, 2 H); uv (hexane) λ_{max} 355 nm (ϵ 28.3). This compound is potentially explosive[58] and should be treated accordingly.

Methylazo-1,1-dimethyl-2-propene (1t). Oxidation of *N*-methyl-*N'*-(1,1-dimethylallyl)sulfonimide was carried out according to Ohme et al.[33] The product was extracted with ether which was washed with water and saturated aqueous NaCl. Removal of the solvent and short path distillation afforded the product in 54% yield: bp 45–50° (30 mm); NMR δ 1.22 (s, 6 H), 3.63 (s, 3 H), 4.90 (m, 2 H), 5.90 (m, 1 H); uv (hexane) λ_{max} 363 nm (ϵ 17.0).

Isopropylazo-1,1-dimethyl-2-propene (2t). A solution of 1.6 g (40 mmol) of NaOH in 15 ml of water was stirred on ice in a 250-ml three-necked Morton flask. A solution of 5.0 g (24.2 mmol) of the sulfonimide in 50 ml of ether was added, and then 75 ml of Clorox (54 mmol of NaOCl) was added all at once with rapid stirring. After 12 min, a KI–starch test showed that all the NaOCl had

been consumed. The usual work-up and short path distillation at 47° (25 mm) gave 1.8 g (53%) of a pale yellow oil: NMR δ 1.18 (d, J = 7, 6 H), 1.22 (s, 6 H), 3.60 (m, J = 7, 1 H), 5.00 (m, 2 H), 5.95 (m, 1 H); uv (hexane) λ_{max} 365 nm (ε 19.0).

***tert*-Butylazo-1,1-dimethyl-2-propene (3t).** The procedure was the same as for **6t** detailed above. Starting with 1.0 g (45 mmol) of the sulfonimide, 455 mg (65%) of a yellow oil was obtained: NMR δ 1.13 (s, 9 H), 1.20 (s, 6 H), 4.90 (m, 2 H), 5.88 (m, 1 H); uv (hexane) λ_{max} 366 nm (ε 20.6).

3-Cyano-3,6-dimethyl-1,2-diazacyclohexene-6 was prepared according to the method of Overberger:[67] yield 100%; NMR ($CDCl_3$) δ 1.50 (s, 3 H), 1.90 (s, 3 H), 1.72–2.50 (m, 4 H), 6.42 (br, 1 H).

3,6-Dicyano-3,6-dimethyl-1,2-diazacyclohexane was prepared by a modification of Overberger's procedure.[36] To a solution of 7.8 g (60 mmol) of NaCN in 100 ml of water was added 5.5 g (40 mmol) of the crude cyclohexene from above. The solution was stirred on ice, while 10 g (0.1 mol) of concentrated H_2SO_4 was added dropwise. After stirring for 18 hr at 25°, the reaction solution was extracted with 4 × 50 ml of CH_2Cl_2. The extracts were dried over Na_2SO_4 and then evaporated to give 5.5 g (84%) of pale yellow oil which crystallized after standing under N_2 for 3 weeks. The white crystals were washed ten times with benzene, pumped dry, and stored in a vacuum desiccator: yield 1.7 g (26%); mp 92.7–94.0° (sealed tube; lit.[36] mp 99–100°); NMR ($CDCl_3$) δ 1.53 (s, 6 H), 1.95 (d of d, J = 5, 2 Hz, 4 H), 3.15 (br, 2 H).

3,6-Dicyano-3,6-dimethyl-1,2-diazacyclohexene-1 (5). The cyclic azoalkane was typically prepared in CH_2Cl_2 or acetone by the addition of 1 ml of 0.06 M *tert*-butyl hypochlorite to 2 ml of a 0.04 M solution of the above hydrazine at −40°. For the thermal kinetics reported, the preparation was carried out at the temperature of the thermostated cell. As followed by uv spectroscopy, the oxidation was instantaneous and clean. A solution of **5** was prepared at −78° in a 2-mm cell and a uv spectrum obtained. Thermolysis of this sample and measurement of the N_2 evolved allowed calculation of the extinction coefficient, λ_{max} (CH_2Cl_2) 388 nm (ε 144).

Determination of Activation Parameters. Trans azoalkanes were thermolyzed in solution (see Table II for solvents) using a constant-volume, variable-pressure kinetic apparatus[37] to monitor nitrogen evolution. Each sample was vacuum degassed prior to the kinetic run. A Bayley temperature controller held the temperature of the silicon oil bath constant to ±0.01°. Bath temperatures were measured using precision mercury thermometers manufactured and calibrated by the Tagliabue Division of Marshallton Mfg. Co. Standard stem corrections were applied. In addition, the two thermometers covering the range 75–155° were checked against a platinum resistance thermometer.

Points read from the plots of pressure vs. time were entered into a least-squares computer program to obtain nitrogen evolution rate constants at each temperature. The experimental infinity reading generally required slight adjustment to minimize the standard deviation of the data points. The rate constants and corrected temperatures were plugged into a computer program which provided activation parameters. The slope of $\ln(k/T)$ vs. T^{-1} was $-\Delta H^{\ddagger}/R$, and the intercept minus 23.76 was $\Delta S^{\ddagger}/R$.

Cis azoalkanes were prepared in situ by uv irradiation of a cold, degassed solution of trans in the gas evolution kinetic apparatus. Chilled acetone from a Sargent water bath cooler was circulated through an aluminum coil in the bottom of an ethanol bath whose temperature was regulated by the Bayley controller connected to a 225-W knife heater. Rates of nitrogen evolution were monitored just as for the trans isomers.

The apparatus used to study compound **5** consisted of a stirred square cell immersed in a boiling liquid. The liquid refluxed from a Dry Ice condenser, and the whole apparatus was enclosed in a vacuum jacket. Since the temperature of the solution under study differed slightly from the reported boiling point of the refluxing liquid, it was monitored independently by means of a calibrated thermistor. The condensable gases employed and their boiling points were: *cis*- + *trans*-2-butene (2.5°), *n*-butane (0.0°), and isobutene (−6.0°). The optical absorbance of **5** was followed with a Cary 17 uv spectrophotometer, and the data were treated as described above.

To demonstrate the absence of induced decomposition of **6t**, a 0.034 M solution of this compound in benzene containing 0.080 M 2,2,6,6,-tetramethylpiperidine-1-oxyl[58] was degassed and sealed in five tubes. Four of these were heated at 53.8° in a regulated oil bath and were removed at various times. The rate of nitroxyl disappearance, which was calculated from its absorbance at 468 nm, corresponded to a half-life of 42 min. A similar experiment using 3.03×10^{-3} M Koelsch radical[58] and 1.53×10^{-3} M **6t** in benzene at 53.1° also gave a half-life of 42 min. The half-lives calculated from the activation parameters in Table IV at these temperatures are 41 and 45 min, respectively. Thus, the presence of efficient radical scavengers does not affect the thermolysis rate of **6t**.

Low temperature irradiation of azoalkanes was carried out in a modified matrix isolation apparatus. A polymethyl methacrylate (PMMA) block containing trans azoalkane was prepared as described in the text and then machined to fit snugly into a hollow aluminum sample holder. The holder was suspended from a liquid nitrogen cooled cold finger and in an evacuated metal housing with quartz windows, and its temperature was monitored by means of a thermocouple. Irradiation of the cold PMMA block produced cis azoalkane, as detected from its characteristic absorption spectrum (cf. Figure 3). Once the absorbance of cis had reached an optimum value, the light was shut off and the liquid nitrogen allowed to evaporate. The absorbance at λ_{max} was then followed as the temperature of the sample slowly rose.

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XXI. Some Mono-, Di-, and Trialkylhydrazyls[1]

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Abstract: The kinetics, mechanism, and products of decay of some mono-, 1,2-di-, and trialkylhydrazyls have been examined. 1-Alkylhydrazyls decay with second-order kinetics at the diffusion-controlled limit. 1,2-Diisopropylhydrazyl undergoes a very rapid second-order decay, which is a β-disportionation to hydrazine and azo compound. According to their structure, trialkylhydrazyls may decay by a fast second-order β-disproportionation (alkyl-H → N) or by a slow β-scission (loss of alkyl and formation of an azo compound). These results, together with previously reported data on 2,2-dialkylhydrazyls,[14] are discussed in relation to the possibilities of isolating persistent alkyl hydrazyl radicals.

Interest in alkyl hydrazyls has grown dramatically in the 2 years since the uv[4] and EPR[5] spectra of the first of these radicals were reported. Attention has been focused primarily on the EPR spectra.[6-13] Apart from the usual qualitative statements about radical lifetimes, detailed kinetic and product studies have been confined to Nelsen and Landis' work on some bi- and multicyclic trialkylhydrazyls[6] and work from this laboratory on a series of 2,2-dialkylhydrazyls.[14] Further work on alkylhydrazyls is clearly justified when it is remembered that amongst arylhydrazyls is included diphenylpicrylhydrazyl (DPPH), one of the most persistent free radicals known.[15] In this paper, we report on the kinetics and products of the decay of some mono-, di-, and trialkylhydrazyls.

Experimental Section

Materials. Methyl hydrazine was obtained from Chemical Intermediates and Research Laboratories, Inc. Benzylhydrazine was prepared from benzyl chloride and hydrazine hydrate.[14] 1,2-Diisopropylhydrazine was obtained from Fluka, AG, and azotrifluoromethane from Merck Sharpe and Dohme, Ltd. *tert*-Butylhydrazine was prepared from chloramine and *tert*-butylamine.[16] Trialkylhydrazines were prepared by reduction of hydrazones with sodium cyanoborohydride.[17] The hydrazones were prepared by condensation of 1,1-dialkylhydrazine with a carbonyl compound. The following preparation of 1-isopropylamino-2,2,6,6-tetramethylpiperidine[18] is fairly typical of a slow and difficult reaction.

A mixture consisting of 2.5 g (0.016 mol) of $TMPNH_2$,[19] 0.9 g (0.016 mol) of acetone, and 0.07 g (0.0007 mol) of 2-hydroxypyridine (a catalyst) was refluxed 48 hr.[20] The reaction mixture was washed with water and ether, and the ether layer was dried and then distilled under vacuum. The hydrazone [$TMPN{=}C(CH_3)_2$] distilled at 85° (12 mm), yield 2.0 g. It was purified by preparative VPC. NMR spectrum in C_6D_6 (in ppm downfield from Me_4Si):[21] TMP, $(CH_3)_2$ 0.84 (s), $(CH_3)_2$ 1.30 (s), $(CH_2)_3$ 1.54 (m, broad), ${=}C(CH_3)_2$ 1.79 (d, J = 4 Hz). Anal. Calcd for $C_{12}H_{24}N_2$ (mol wt 196.34): C, 73.41; H, 12.32; N, 14.27. Found (mol wt (mass spectrometry) 196): C, 73.37; H, 12.30; N, 14.35.

To a stirred solution of 1.2 g (0.006 mol) of $TMPN{=}C(CH_3)_2$ in 25 ml of acetonitrile was added 0.2 g (0.003 mol) of $NaBH_3CN$ in 4 or 5 small portions over 30 min. After a further 45 min, ca. 1 ml of acetic acid was added slowly and the reaction mixture stirred for an additional 6 hr. Then 0.6 ml of concentrated HCl was added, the acetonitrile removed under vacuum, and the oily residue dissolved in 20 ml of H_2O, basified with KOH, saturated with NaCl, extracted with ether, and dried over $MgSO_4$. The ether was removed and the yellow oil distilled under high vacuum on a molecular still at room temperature (yield of $TMPNHCH(CH_3)_2$, 0.5 g). NMR spectrum in C_6D_6: TMP, $(CH_3)_4$ and $(CH_2)_3$ three broad peaks at 0.93, 1.14, and 1.43; $CH(CH_3)_2$ 1.01 (d, J = 6 Hz), $CH(CH_3)_2$ 3.14 (septet); NH 2.30 (broad). Anal. Calcd for $C_{12}H_{26}N_2$ (mol wt. 198.35): C, 72.66; H, 13.21; N, 14.12. Found