Chemical Reviews

Mechanism of the Thermal and Photochemical Decomposition of Azoalkanes

PAUL S. ENGEL

Department of Chemistry, Rice University, Houston, Texas 77001
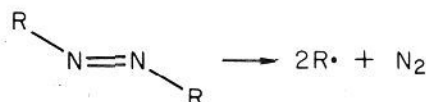
Contents

I. Introduction

Although azoalkanes have been known since 1909,[1] it is only during the past 10 years that the richness of their chemistry has become apparent.[2] These versatile compounds lose nitrogen thermally or photochemically under a wide variety of conditions;

$$R-N=N-R \longrightarrow 2R\cdot + N_2$$

hence, they are probably the cleanest and most convenient sources of radicals and biradicals of nearly any desired structure. Since several reviews on azoalkanes are available,[3-8] I shall be concerned primarily with the more recent work in the field, especially the mechanism of azoalkane homolysis. Literature coverage, though not exhaustive, should be reasonably complete for the period 1972 to mid-1979.
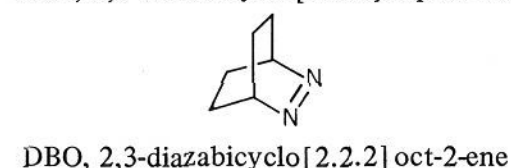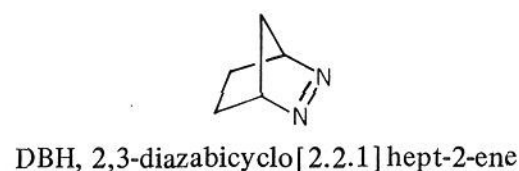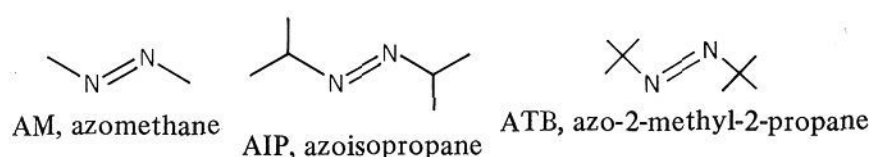
Because there are so many kinds of azo compounds, this review will have to be restricted to azoalkanes, that is, to molecules in which nitrogen is bonded to saturated carbon. Some interesting compounds which will not be included are tetrazenes,[9] azosilanes,[10] aromatic azo compounds,[11,12] and α-carbonyl azo compounds.[13,14] Unsaturation may be present elsewhere in the molecules covered, but for brevity, such
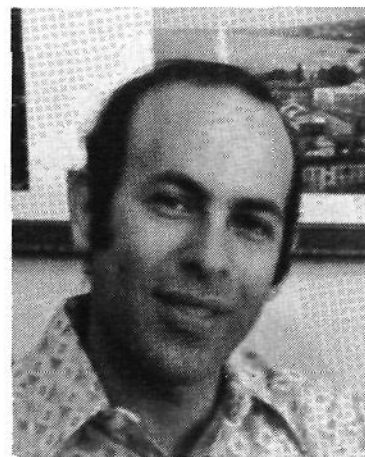
Paul Engel was born in Pittsburgh and was educated in Los Angeles. At the age of 14, his primary interest switched from electronics to chemistry. After receiving a B.S. degree at UCLA, he joined P. D. Bartlett's group at Harvard and obtained a Ph.D. in 1968. Dr. Engel then spent 2 years at the National Institutes of Health in Bethesda, MD, after which he joined the Rice University faculty. He became Associate Professor of Chemistry in 1975 and was awarded an Alfred P. Sloan Fellowship the same year. Although he has published 26 papers on various aspects of azoalkane chemistry, he has also worked on the photochemistry of β,γ-unsaturated ketones and is presently interested in free radicals and peroxides. Outside of chemistry, Dr. Engel's main interest is playing the bassoon.

compounds will also be classified as azoalkanes. The 1,2-diazene nomenclature, which has advantages in some cases, will not be employed here. Most of the azoalkanes which have been used recently to synthesize interesting organic compounds and to generate short-lived intermediates will also be discussed. Finally, the author believes that this attempt to collect the known activation parameters and quantum yields for azoalkanes will be of value to future workers in the field.

The five azoalkanes mentioned most frequently throughout this review will be abbreviated as shown below. The other
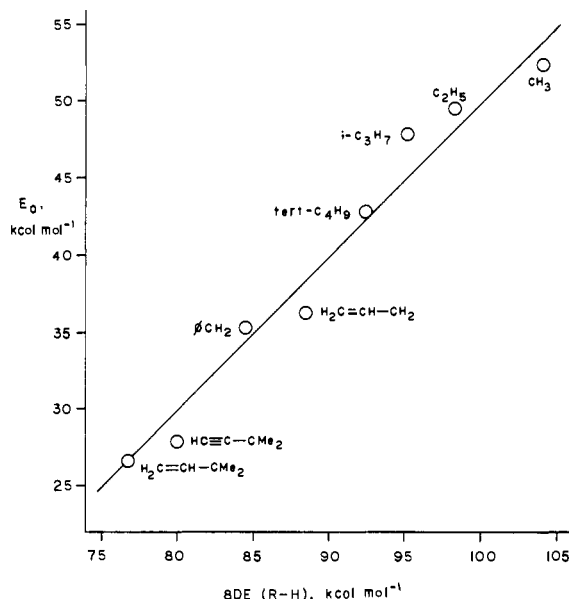
AM, azomethane

AIP, azoisopropane

ATB, azo-2-methyl-2-propane

DBH, 2,3-diazabicyclo[2.2.1]hept-2-ene

DBO, 2,3-diazabicyclo[2.2.2]oct-2-ene

Figure 1. Polanyi plot of activation energy for thermolysis of symmetrical azoalkanes vs. bond dissociation energy of the corresponding hydrocarbon. A line of unit slope is shown. Values of E_a are taken from Table I while BDE's, with the exceptions of dimethylallyl[20,21] and dimethylpropargyl,[21,22] are taken from ref 19.

compounds, most of which are included in Tables I, II, VIII, and XI, will be referred to by number. Other abbreviations are as follows: ISC = intersystem crossing, RDP = residual direct photolysis (cf. IV.A.1.c), SCE = spin correlation effect, Φ_r = quantum yield for nitrogen formation.

II. Thermal Reactions

A. Acyclic Azoalkanes

#### 1. Effect of Structure on Thermolysis Rate

Table I lists activation parameters for thermolysis of most of the symmetrical acyclic azoalkanes which have been reported to date. When rate-temperature data were given, the activation parameters were often recalculated in order to facilitate comparison between different studies. It is apparent that the thermal stability of azoalkanes depends strongly on the ability of the attached R groups to sustain an unpaired spin. Thus, azobenzene (162t; t designates trans) is stable at 600 °C[15] whereas azotriphenylmethane (163) has only a transient existence even
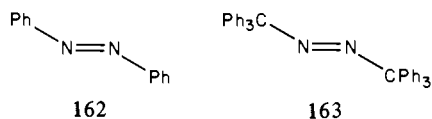
at –40 °C.[16,17] Al-Sader and Crawford[18] first pointed out that a Polanyi plot of R–H bond dissociation energy vs. E_a for azoalkane (RNNR) thermolysis is linear. As seen in Figure 1, an updated version of this plot is still essentially linear, but due to uncertainties in both BDE[19] and E_a, it shows considerable scatter. For the sake of simplicity, I have selected representative values of these parameters rather than including all available data (cf. Table I). The fact that the slope of Figure 1 is approximately unity suggests that one C–N bond is completely broken or that both bonds are partly broken in the transition state for azoalkane homolysis. This distinction will be considered in section II.A.2.

In view of the strong dependence of azoalkane thermolysis rates on incipient radical stability, it seems reasonable that a study of substituted azoalkanes might produce a scale of rad-

ical-stabilizing ability analogous to the Hammett σ scale for ionic reactions. Table I includes data for two such attempts using benzylic azo compounds (164a–c).[23,24] Although the effect of

164a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = Me$
c, $R_1 = R_2 = Me$
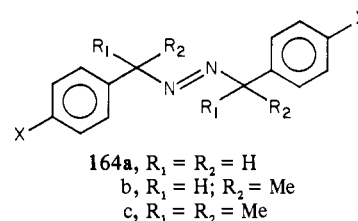
X on thermolysis rate is disappointingly small, one can conclude that unlike peresters,[4] azoalkanes are not subject to polar effects. A question which remains unanswered is why azotoluenes (164a) show even less sensitivity to the nature of X than do azocumenes (164c).[23]

If the group X is placed directly on the α carbon (cf. 165) its influence on decomposition rate is very much larger.[23,25]
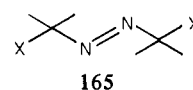

165

Table I includes activation parameters for a wide variety of substituents X, determined mostly by Timberlake and co-workers.[23,25,26] As expected, resonance stabilizing groups[27,28] are the most effective rate accelerators, but sulfur on the α carbon also has a large effect. The highly negative $\Delta S^{\ddagger}$ in sulfur compounds (12 and 97) as well as the abnormal thermolysis products[26] point to an unusual and still unknown decomposition mechanism.

Rate constants for azoalkane thermolysis have been used to assess the influence of ring size on radical stability. Results for azonitriles 166[29] and α-methylcycloalkylazo compounds 167[30]

166

167
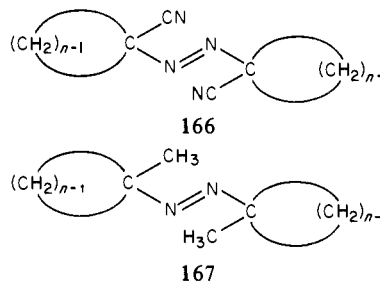
are shown in Figure 2. As pointed out by Rüchardt,[30] the observed trend parallels that found in solvolysis of the analogous cycloalkyl halides, providing further evidence that the transition state for azoalkane thermolysis is geometrically similar to the planar radicals which are produced.

An attempt to generate cyclopropyl radicals by azoalkane thermolysis resulted instead in vinylcyclopropane rearrangement (98 → 168).[31] Similarly, stereoisomers 169 and 170 were

98

168
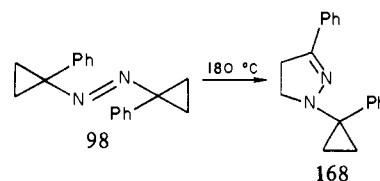
equilibrated by heating to 130–152 °C and were rearranged to pyrazoline 171 via diradical 172.[32] It would be of interest to see whether pyrazoline would still form during decomposition of 173 in which cleavage of the triphenylmethyl moiety should be very facile.[16,17] Since cyclopropyl radicals have been
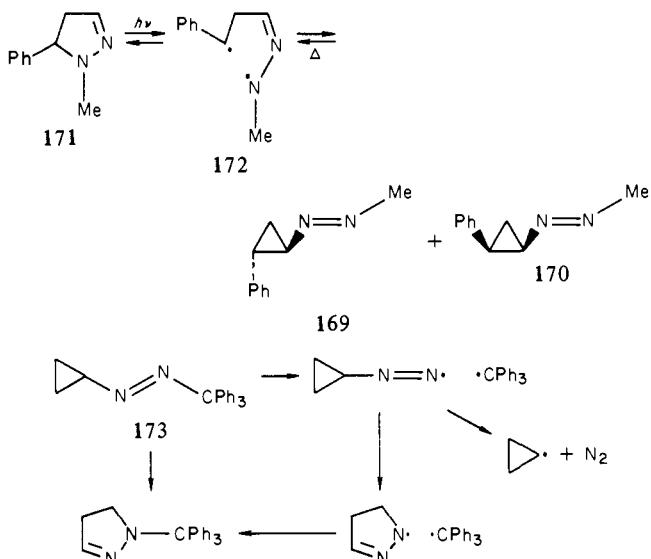
generated from thermolysis of peresters,[31,33] one might expect the cyclopropyldiazenyl radical to lose nitrogen. On the other hand, this species might rearrange to a pyrazolinyl radical, as was suggested in the case of (trifluoromethyl)azocyclopropane.[34]

Recently, a series of azoalkanes (**17, 44, 45, 63**) was used to look for differences in stability of constrained allylic radicals.[35]

17 (1.0)   **44 (1.77)**

45 (4.07)   **63 (3.36)**

$(k_{rel}, 50 \ ^\circ C)$

The relative rate constants at 50 °C shown above imply similar delocalization energy in all cases, despite the geometric distortion of the 2-(1-cyclobutenyl)-2-propyl radical. However, the small rate enhancement by γ-ethyl groups in **44** contrasts wit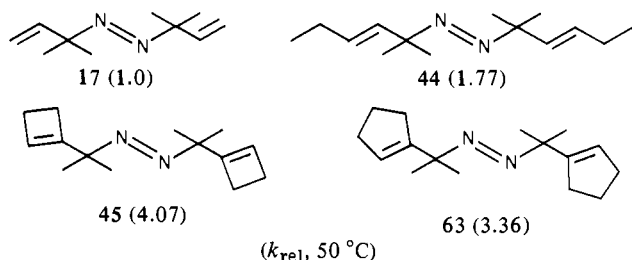h the large effect of α-methyl groups on thermolysis of 1-azo-2-propene (**3**).[35] Apparently a saturation effect[36] comes into play when more than two alkyl groups are present. To test this explanation would require study of other allylic azoalkanes. Of greater interest would be the use of azoalkanes to probe the stability of more highly conjugated radicals **174–176** since de-

174   **175**   **176**
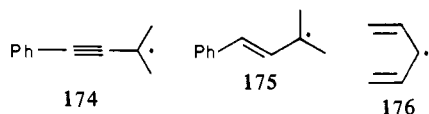
composition kinetics of the appropriate peresters[37,38] are not only less sensitive to radical stability but also might be complicated by polar effects.[4]

Besides incipient radical stability, the other important influence on azoalkane thermolysis rates is ground-state strain. Overberger and co-workers[39] were the first to report this effect in the acyclic series; for example, their most hindered compound (**72**) decomposed about 100 times faster than azoisobutyronitrile (**10**). With the discovery of a new synthetic method for preparing hindered azoalkanes,[40,41] Timberlake and co-workers were able to extend these studies to such compounds as **56** and **139**. Thus **56** undergoes thermolysis over 1300 times faster than ATB at 100 °C, even though a *tert*-octyl radical should be of similar stability to a *tert*-butyl radical.[23] Thermochemical measurements on these two azoalkanes demonstrate that the increased lability of **56** is accounted for quantitatively by its ground-state steric
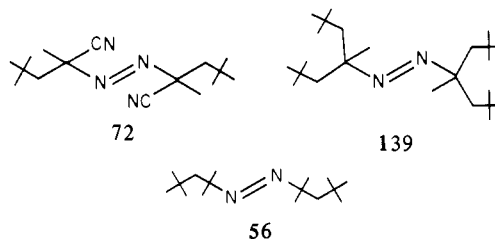
strain.[42] **139** is the most strained acyclic azoalkane yet prepared, its thermolysis rate being 57 000 times that of ATB[43] Taking advantage of another new azoalkane synthesis,[44] Duismann and Rüchardt[45] made an extensive study of steric acceleration of azoalkane thermolysis and found that, as in azocycloalkanes (see above), the rate of nitrogen loss is directly related to that of the corresponding solvolysis reaction. For **164** (X = H), larger R groups actually slowed down homolysis, demonstrating that steric inhibition of resonance was slightly more important than acceleration caused by greater back-strain.[46]

Despite the success of incipient radical stability and ground-state strain in rationalizing the thermal lability of azoalkanes, studies of bridgehead azoalkanes exhibit some discrepancies. Figure 3 compares the various methods which have been devised to assess bridgehead radical stabilities.[47-57] Although the poor agreement among these methods suggests that our knowledge of bridgehead radical stabilities is only qualitative, the slow rate of 1-azoadamantane (**112**) homolysis[47,58] relative to that of ATB is particularly striking. A comprehensive study of bridgehead azoalkanes[47] shows that a ponderal effect is not responsible for this difference because both azohomoadamantanes (**129, 130**) decompose faster than azoadamantane. Even if the other studies[48-56] do not reflect true radical stability on account of their early transition state,[59] azoalkane thermolysis rates correlate only in a crude manner with the calculated enthalpy difference (ΔH) between hydrocarbon and carbenium ion[80] (cf. Figure 4). The values of ΔH do correlate with log k for solvolysis and were also suggested to reflect bridgehead radical stability.[60] Although the slower rate of azoadamantane relative to ATB is explicable in part by the higher energy of adamantyl radicals, the nonlinearity in Figure 4 could be due to a change in decomposition mechanism.[47] The five compounds at the top of Figure 4 which are "too fast" might decompose concertedly, whereas the slower ones could lose nitrogen stepwise (see discussion below). However, the reason behind this change in mechanism is not obvious, and a study of unsymmetrical azoalkanes designed to test this idea led to no consistent picture.[47]

Although the above discussion is based only on rate constants, it should be noted that the reported[47] activation parameters for azo-1-norbornane (**42**) are in error. The correct $\Delta S^\ddagger$ derived from the given rate constants is -3.1 eu, which stands in remarkable contrast to the value of 31.5 eu reported[58] for azoadamantane. This discrepancy probably reflects the fact that these pyrolyses are neither clean nor easy to monitor.

2. One-Bond vs. Two-Bond Cleavage

The question of whether azoalkanes lose nitrogen by simultaneous breakage of both C–N bonds (a) or whether they proceed via a diazenyl radical (b) was asked as early as 1929.
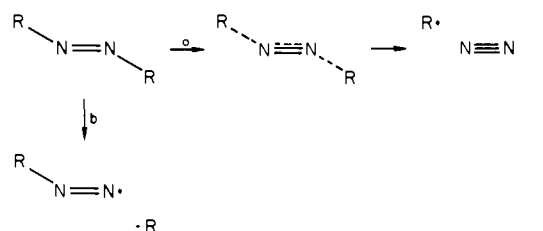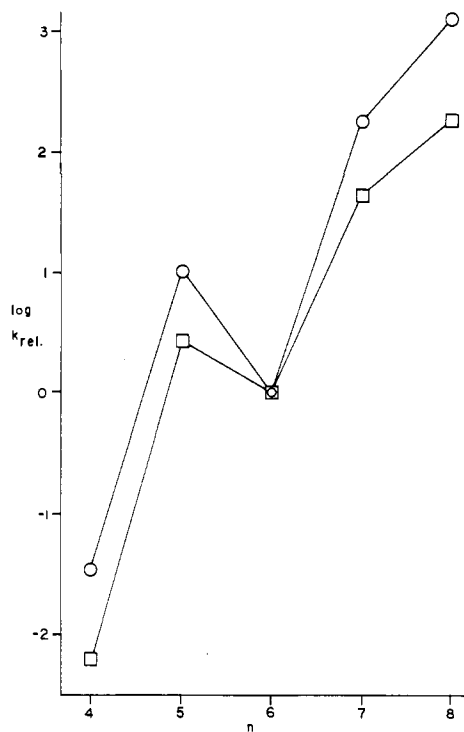
Figure 2. Relative rate constants for **166** (80 °C in toluene, (O))[29] and **167** (200 °C in benzene, (□))[30] as a function of ring size (n).
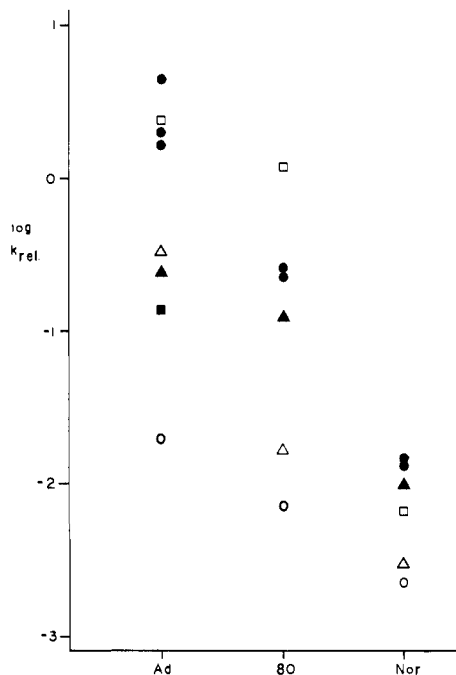

Figure 3. Relative rate constants for bridgehead radical formation by various methods: (O) azoalkane thermolysis,[47] (●) perester thermolysis,[48-51] (△) ketone photolysis,[52] (▲) stannane reduction of halides,[53] (□) decarbonylation,[48,54] (■) β-scission of oxy radicals.[55,56] k for tert-butyl is assigned a value of 1.0. Ad = 1-adamantyl, BO = bicyclo-[2.2.2]oct-1-yl, Nor = 1-norbornyl.

Ramsperger compared the E_a for decomposition of AM, **117**, and AIP and concluded that since the value for the unsymmetrical compound fell between that of the two symmetrical compounds, both C–N bonds break at once. Unfortunately the
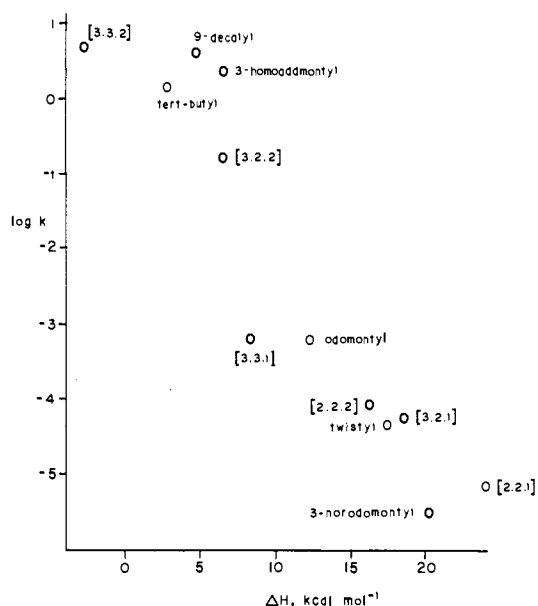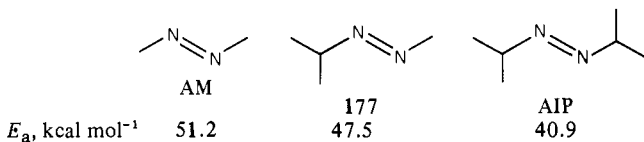
	AM	177	AIP
E_a, kcal mol^{-1}	51.2	47.5	40.9

Figure 4. Correlation of log k (s^{-1}) for azoalkane (RN$_2$R) homolysis[47] with the calculated enthalpy difference (ΔH) between hydrocarbon (RH) and carbenium ion (R$^+$).[60] ΔH for tert-butyl is taken from: Gleicher, G. J.; Schleyer, P. v. R. J. Am. Chem. Soc. **1967**, 89, 582. Numbers in brackets indicate the size of bridgehead bicyclic azoalkanes and carbenium ions.

activation energy for AIP used by Ramsperger is incorrect, the best current value being 47.9 kcal mol^{-1}.[62] If the value for **177** is reliable, these results would point toward one-bond scission.

Since Ramsperger's early work, much effort has been expended in trying to decide between mechanisms a and b for azoalkane thermolysis.[3,4,63-65] Advances in the synthesis of unsymmetrical azoalkanes (Table II) have allowed the Ramsperger criterion to be applied to a number of other compounds. Table III is a compilation of free energies for the thermolysis of unsymmetrical azo compounds compared to their more stable and less stable symmetrical analogues ($\Delta\Delta G_1^{\ddagger}$ and $\Delta\Delta G_2^{\ddagger}$, respectively). Free energies of activation are used because more of them are available and because they are more accurate than the Arrhenius E_a's. Mechanism b suggests that the nature of the less-stable free radical R$_1$ should have no effect on $\Delta G^{\ddagger}$ for thermolysis of R$_1$N=NR$_2$ so that $\Delta\Delta G_2^{\ddagger}$ should be zero. Replacing a tert-butyl group in ATB by a cumyl group, for example, lowers $\Delta G^{\ddagger}$ by 8.4 kcal mol^{-1}. If mechanism b obtained, similar replacement of the other tert-butyl group should leave $\Delta G^{\ddagger}$ unchanged, but instead it is lowered by an additional 3.3 kcal mol$^{\Delta}$. In general, $\Delta\Delta G_2^{\ddagger}$ is less than $\Delta\Delta G_1^{\ddagger}$, but only in a few cases[65,66] does $\Delta\Delta G_2^{\ddagger}$ equal zero. The fact that $\Delta G^{\ddagger}$ for thermolysis of an unsymmetrical azoalkane lies closer to that of its less stable symmetrical counterpart (R$_2$N=NR$_2$) suggests more R$_2$–N bond breaking than R$_1$–N bond breaking in the transition state.[27,64] Thus, a symmetrical azoalkane cleaves by mechanism a whereas greatly different R groups lead to unequal stretching of the two C–N bonds. In the extreme case of arylazoalkanes ArN=NR, the evidence[67,69] is overwhelmingly in favor of one-bond scission.

A thermochemical-kinetic approach[42] has been employed to argue against the stepwise cleavage mechanism. As seen in Figure 5, the sum of the experimentally determined ground-state strain and $\Delta H^{\ddagger}$ for thermolysis of ATB, **56**, and **195** is constant at ~42.5 kcal mol^{-1}. The simplest description of the transition state consistent with this picture is one having both C–N bonds broken, thereby relieving all nonbonded interactions in **56** and **195**. Stepwise breaking of the tert-octyl–N bond in these two compounds leaves the radicals tert-butyl-N=N· and tert-octyl-N=N·, of which the latter would surely be more strained. One-bond cleavage therefore predicts a higher $\Delta H^{\ddagger}$ for **195** than
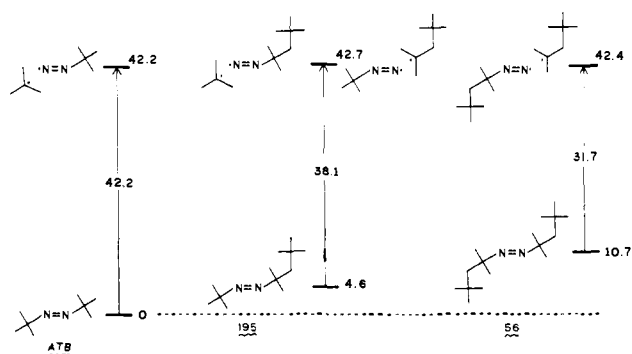
Figure 5. Enthalpy of ground state ATB, **56**, **195** and their products of one-bond cleavage. Strain energies are experimental values relative to ATB and the vertical arrows are experimental $\Delta H^{\ddagger}$'s (kcal mol^{-1}).[42]

for **56**, inconsistent with the observed values.

A variety of other techniques have been employed to distinguish one-bond from two-bond cleavage in azoalkanes, but since these results have been reviewed[3,4,63] we shall consider only the most recent work. Irradiation of **221t** at −125 °C gave the cis isomer **221c**, which decomposed on warming to −36 °C. [15]N CIDNP revealed enhanced absorption in both cis and trans starting material and emission from molecular nitrogen.[70]
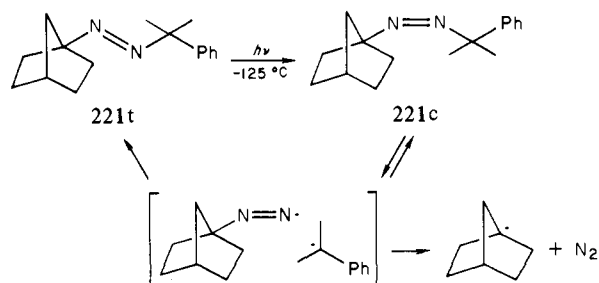

Analogy with earlier work on phenylazoalkanes[67] demonstrated the transient existence of 1-norbornyldiazenyl radical and hence the one-bond mechanism for **221c**. Because **221c** is highly unsymmetrical, stepwise cleavage is reasonable, but it remains to be seen whether this elegant technique of ^{15}N CIDNP will prove fruitful for simple alkyldiazenyl radicals. The only other evidence for an alkyldiazenyl radical is the case of CH₃—N=N· produced by thermolysis of another highly unsymmetrical azoalkane, **180**.[71]
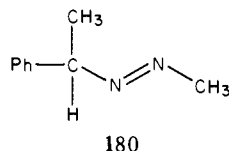

In summary, azoalkane thermolysis seems to proceed by a continuum of mechanisms between a and b; the more unsymmetrical the azo compound, the more unsymmetrically it cleaves.

3. Thermolysis Products

Azoalkane thermolysis has often been used to study the behavior of caged radical pairs. In a classic series of papers, Hammond and co-workers[72] examined the fate of α-cyanoalkyl radicals produced by thermolysis of azonitriles. Later work in this area centered on the stereochemistry of free-radical recombination.[73,74] Optically active azo-α-phenylethane (**64**), for
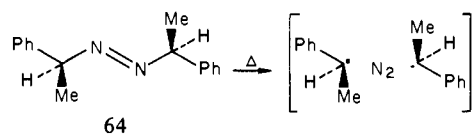
example, led to the following relative rate constants for caged α-phenylethyl radicals: rotation 15, diffusion 2.4, recombination 1.0, disproportionation 0.14.[73] The relative importance of recombination and disproportionation as a function of radical structure has been evaluated by using a series of azoalkanes.[75] Another approach to the problem of competing processes in caged radical pairs employed the thermolysis of **17**.[76] The
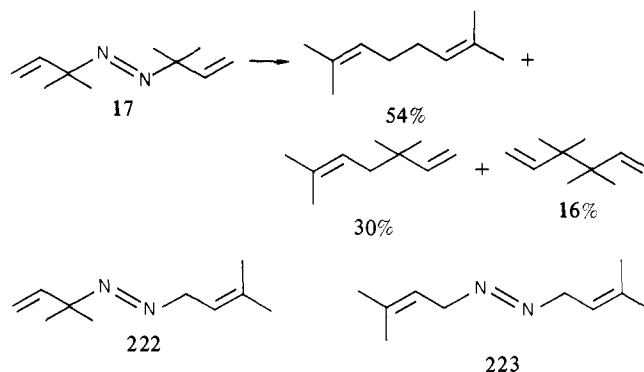
presence of all three diene products in scavenged runs and the fact that azoalkanes **222**[77] and **223**[78] gave approximately the same product composition as **17** support the idea that rotation within the solvent cage is much faster than recombination. Efficiencies of radical production and rates of azoalkane thermolysis decrease at high external pressure;[79] in fact, the activation volumes obtained from such studies are part of the evidence for two-bond homolysis of symmetrical azoalkanes.[80] Since many of the other cage effect studies employed photolysis of azoalkanes, discussion of these results will be deferred until section IV.B.

4. Acyclic cis-Azoalkanes

Whereas irradiation of *trans*-azobenzene (**162t**) has long been known to produce the cis isomer,[81] it was only in 1964 that this process was discovered for an aliphatic azo compound, azomethane (AM).[82] Since that time, AM(c) has been characterized
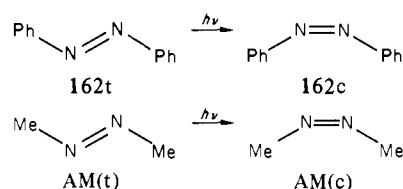
by Raman[83] and microwave[84] spectroscopy as well as by the methods summarized in Table IV. *cis*-Azomethane can be prepared either by the photoisomerization route or by a pyrolytic retrograde Diels–Alder reaction.[85] With respect to physical and
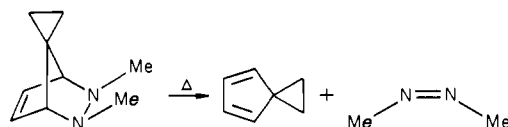
chemical properties, AM(c) and AM(t) are prototypes for the higher azoalkanes. Thus λ_{max} for the cis isomer is always longer and ϵ is always higher than that for trans.[86] When an α hydrogen is present, tautomerization to the more stable hydrazone is a much more serious problem in the cis isomer than it is in the trans.[82,83] The tautomer of AM (**224**) is said to dimerize,[87] which
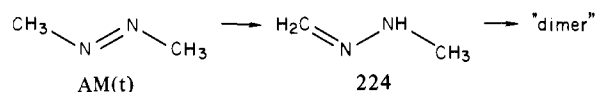
would explain why crystals form on the walls of old gaseous AM

TABLE I. Activation Parameters for Thermolysis of Symmetrical Acyclic *trans*-Azoalkanes $(R_1 R_2 R_3 CN{=}NCR_1 R_2 R_3)^a$

R_1, R_2, R_3	compd	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	E_a, kcal mol^{-1}	log A	solvent	notes	ref
H$_3$	AM			51.2	15.7	g	nrd	b
				55.4	17.3	g	NO inhibited; 3 p	c
				52.4	16.5	g		d
				52.5	16.55	g		e
				50.2	15.9	g		f
F$_3$	1			55.2 ± 0.4	16.2 ± 0.2	g	nrd	g
				48.5	13.9	g		h
Me, H$_2$	2			47.2	15.1	g	nrd	i
				48.5	15.77	g	nrd	j
				49.7	16.4	g		62
				44.5	14.2	g	toluene carrier	k
CH$_2$=CH, H$_2$	3	35.3 ± 0.2	10.0 ± 0.5	36.1	15.54	g	r	18
		30.8 ± 0.4	0.3 ± 0.9			Ph$_2$O		l
Et, H$_2$	4			45.7	14.6	g	nrd	m
Me$_2$, H	AIP	39.5 ± 0.6	0.8 ± 1.0	40.7 ± 0.6	13.67 ± 0.23	g	r	n
				51.9	18.14	g	nrd	o
				40.75	13.68	g	nrd	m
				47.9	16.6	g		62
MeC(NO$_2$)$_2$, H$_2$	5	$k = 1.3 \times 10^{-4}$ s^{-1} at 179 °C						p
Me$_2$, Cl	6	38.9 ± 1.3	12.0 ± 2.7	39.5 ± 1.3	15.94 ± 0.60	Ph$_2$O–iq	6 p, r	25
n-C$_3$H$_7$, H$_2$	7			53.2 ± 0.6	17.71	g	helium carrier	q
Et, Me, H	8			48.4 ± 0.6	17.28	g	helium carrier	q
i-Pr, H$_2$	9			49.0 ± 0.5	16.23	g	helium carrier	q
Me$_3$	ATB			43.0 ± 0.5	17.15	g	helium carrier	q
				42.8	15.34	g		r
		42.1 ± 0.3	16.3 ± 0.6	43.1 ± 0.3	16.96 ± 0.13	Ph$_2$O–iq	6 p, r	s
		43.7	17			C$_6$H$_6$	nrd	64
				42.8	16.4	g		62
		41.2 ± 0.6	13.1 ± 1.2	42.2 ± 0.6	16.3 ± 0.3	g	toluene carrier	k
		43.1 ± 0.4	17.4 ± 1.0	44.1 ± 0.4	17.21 ± 0.22	hexadecane	4 p, r	t
Me$_2$, CN	10			31.3			nrd	u
				30.7	15.0	C$_6$H$_6$		v
		31.9	14.2			N-methyl-propionamide	5° range	w
		30.1	9.2			N,N-dimethyl-aniline	5° range	w
				31.1	15.43	PhMe	nrd	x
		33.4	18.5	34.2	17.33	PhMe	2 p, r	y
MeO, Me$_2$	11	40.9 ± 0.8	17.7 ± 1.8	41.9 ± 0.8	17.26 ± 0.40	Ph$_2$O	7 p, r	23
MeS, Me$_2$	12	21.5 ± 1.3	−20.7 ± 3.2	22.3 ± 1.3	8.82 ± 0.69	Ph$_2$O	7 p, r	23
NCO, Me$_2$	13	36.5 ± 1.2	12.4 ± 2.9	37.4 ± 1.2	16.08 ± 0.64	Ph$_2$O	6 p, r	25
H$_2$NCO, Me$_2$	14	29.0 ± 1.3	1.4 ± 3.5	29.8 ± 1.3	13.64 ± 0.76	HO(CH$_2$)$_2$OH	6 p, r	25
Et, Me$_2$	15	42.7 ± 0.2	16.9 ± 0.4	43.5 ± 0.2	17.10 ± 0.08	hexadecane	4 p, r	t
		42.1 ± 0.4	16.0 ± 1.0			PhEt	3 p	107
HC≡C, Me$_2$	16	26.8 ± 0.5	6.7 ± 1.4	27.4 ± 0.5	14.72 ± 0.31	xylene	5 p	27
H$_2$C=CH, Me$_2$	17	26.1 ± 0.8	5.0 ± 2.4	26.8 ± 0.8	14.34 ± 0.54	xylene	5 p	27
		25.6 ± 0.3	3.4 ± 0.8			decane	5 p	35
c-(CH$_2$)$_3$, Me	18	50.7 ± 1.0	22.0 ± 1.9	51.7 ± 1.0	18.28 ± 0.42	C$_6$H$_6$	3 p, r	30
c-(CH$_2$)$_3$, CN	19	30.6 ± 1.2	−2.7 ± 2.8	31.4 ± 1.2	12.77 ± 0.62	PhMe	3 p, r	z
Et, Me, CN	20	32.2 ± 0.3	13.7 ± 0.8	33.0 ± 0.3	16.31 ± 0.18	PhEt	3 p, r	107
		30.2	7.8	30.8	14.99	PhMe	2 p	y
MeOOC, Me$_2$	21			29.3	14.1	decalin	nrd	x
MeCOO, Me$_2$	22	40.9 ± 1.2	10.5 ± 2.6	41.9 ± 1.2	15.72 ± 0.56	Ph$_2$O	7 p, r	23
MeCOS, Me$_2$	23	35.8 ± 0.8	11.8 ± 1.9	36.6 ± 0.8	15.95 ± 0.41	Ph$_2$O	7 p, r	23
n-C$_3$H$_7$, Me$_2$	24	40.7 ± 0.8	14.0 ± 1.7	41.5 ± 0.8	16.46 ± 0.37	hexadecane	5 p, r	t
i-C$_3$H$_7$, Me$_2$	25	$k = 3.06 \times 10^{-4}$ s^{-1} at 180 °C				PhEt		45
Et$_2$, Me	26	$k = 1.91 \times 10^{-4}$ s^{-1} at 180 °C				PhEt		45
c-(CH$_2$)$_4$, Me	27	41.8 ± 0.3	16 ± 1			PhEt	3 p	aa
c-(CH$_2$)$_2$CH, Me$_2$	28	37.7 ± 0.4	12.1 ± 0.9	38.5 ± 0.4	16.02 ± 0.19	Ph$_2$O–iq	6 p, r	s
c-(CH$_2$)$_4$, OMe	29	31.7 ± 0.6	−3 ± 1			PhEt	4 p	aa
c-(CH$_2$)$_2$CH, Me, CN	30	27.7 ± 0.4	8.4 ± 1.2	28.4 ± 1.2	15.09 ± 0.27		r	bb
	30a	24.8 ± 1.2	−0.8 ± 3.6	25.4 ± 0.1	13.09 ± 0.77		r, diastereomer	bb
n-C$_3$H$_7$, Me, CN	31	31.6	13.5	32.4	16.25	PhMe	2 p	y
i-C$_3$H$_7$, Me, CN	32	31.0	10.5	31.6	15.58	PhMe	2 p	y
								cc
c-(CH$_2$)$_2$N=C−NH, Me$_2$	33	29	7			Me$_2$SO–cumene		cc
i-C$_3$H$_7$, Et, CN	34	$k = 1.01 \times 10^{-4}$ s^{-1} at 80.5 °C				PhMe		39
EtOOC, Me$_2$	35		4.8	29.4		PhCl	2 p	dd
MeCOCH$_2$, Me$_2$	36	44.3 ± 1.1	24.1 ± 2.5	45.1 ± 1.1	18.63 ± 0.54	Ph$_2$O	6 p, r	25
Me$_2$CHCH$_2$, Me$_2$	37	$k = 7.66 \times 10^{-4}$ s^{-1} at 180 °C				PhEt		45
Me$_3$C, Me$_2$	38	$k = 5.41 \times 10^{-4}$ s^{-1} at 180 °C				PhEt		45
		40.9 ± 0.2	16.2 ± 0.6	41.7 ± 0.2	16.92 ± 0.12	PhMe	4 p, r	t
		36.8 ± 1.6	6.9 ± 3.5	37.8 ± 0.76	14.92 ± 0.76	Ph$_2$O	7 p, r	23
i-C$_3$H$_7$, Et, Me	39	$k = 5.46 \times 10^{-4}$ s^{-1} at 180 °C				PhEt		45
Et$_3$	40	$k = 3.72 \times 10^{-4}$ s^{-1} at 180 °C				PhEt		45

TABLE I (Continued)

R_1, R_2, R_3	compd	$\Delta H^{\ddagger}$, kcal mol⁻¹	$\Delta S^{\ddagger}$, eu	E_a, kcal mol⁻¹	log A	solvent	notes	ref
c-(CH$_2$)$_5$, Me	41	41.6 ± 0.2	13 ± 1			PhEt	3 p	aa
1-norbornyl	42	45.9 ± 2.2	−3.1 ± 3.4	47.3 ± 2.2	12.88 ± 0.74	C$_6$H$_6$	4 p, error: see II.A.1	47
exo-2-norbornyl	43	$k = 8.14 \times 10^{-5}$ s⁻¹ at 200 °C						ee
endo-2-norbornyl	43a	35.4 ± 2.6	−7.1 ± 5.0					ee
EtCH=CH, Me$_2$	44	27.4 ± 0.5	9.6 ± 1.4	28.1 ± 0.5	15.36 ± 0.31	decane	5 p	35
1-cyclobutenyl, Me$_2$	45	26.8 ± 0.3	9.1 ± 1.1	27.4 ± 0.3	15.25 ± 0.23	decane	7 p	35
c-(CH$_2$)$_5$, OMe	46	46.8 ± 1.5	27 ± 3			PhEt	4 p	aa
c-(CH$_2$)$_4$, OCOMe	47	44.2 ± 1.4	16 ± 3			PhEt	5 p	aa
C$_6$H$_5$, H$_2$	48	33.6 ± 1.1	4.0 ± 2.6	34.6 ± 1.2	14.26 ± 0.58	Ph$_2$O	7 p, r	23
p-ClC$_6$H$_4$, H$_2$	49	35.0 ± 1.5	8.1 ± 3.6	36.0 ± 1.5	15.16 ± 0.77	Ph$_2$O	7 p, r	23
n-C$_4$H$_9$, Me, CN	50	$k = 1.58 \times 10^{-4}$ s⁻¹ at 80.2 °C				PhMe		y
Me$_2$CHCH$_2$, Me, CN	51	28.8	8.4	29.6	15.13	PhMe	2 p, r	bb
	51a	27.8	5.9	28.4	14.57	PhMe	diastereomer 2 p, r	bb
i-C$_3$H$_7$, Et, CN	52	$k = 1.01 \times 10^{-4}$ s⁻¹ at 80.5 °C				PhMe		39
Me$_3$C, Me, CN	53	34.4 ± 0.4	19.6 ± 1.2	35.2 ± 0.4	17.64 ± 0.27	PhMe		bb
	53a	29.6	7.0	30.4	14.83	PhMe	diastereomer 2 p, r	bb
c-(CH$_2$)$_5$, CN	54	35.0 ± 1.1	16.2 ± 3.2	35.6 ± 1.1	16.85 ± 0.68	PhMe	9 p, r	z
c-(CH$_2$)$_3$CH, Me, CN	55	$k = 1.51 \times 10^{-4}$ s⁻¹ at 80.5 °C				PhMe		ff
Me$_3$CCH$_2$, Me$_2$	56	32.0 ± 0.7	2.9 ± 1.7	32.8 ± 0.7	14.00 ± 0.38	Ph$_2$O	7 p, r	23
		34.6 ± 0.1	9.5 ± 0.1	35.4 ± 0.1	15.44 ± 0.1	PhMe	4 p, r	t
[c-(CH$_2$)$_2$CH]$_2$, H	57	35.6 ± 0.2	12.1 ± 0.4	36.4 ± 0.2	16.00 ± 0.10	Ph$_2$O–iq	7 p, r	s
c-(CH$_2$)$_6$, Me	58	38.2 ± 0.4	13 ± 1			PhEt	3 p	2
2-(2-exo-methylnorbornyl)	59	$k = 3.1 \times 10^{-5}$ s⁻¹ at 200 °C				C$_6$H$_6$		64
2-(2-endo-methylnorbornyl)	60	$k = 2.11 \times 10^{-3}$ s⁻¹ at 200 °C				C$_6$H$_6$		64
1-bicyclo[2.2.2]octyl	61	$k = 7.6 \times 10^{-5}$ s⁻¹ at 300 °C				C$_6$H$_6$		47
1-bicyclo[3.2.1]octyl	62	$k = 5.4 \times 10^{-5}$ s⁻¹ at 300 °C				C$_6$H$_6$		47
1-cyclopentenyl, Me$_2$	63	27.8 ± 0.6	12.2 ± 1.8	28.6 ± 0.6	15.93 ± 0.39	decane	6 p	35
Ph, Me, H	64	29.6	0.6	30.4	13.46	p-cymene	2 p	24
		32.6 ± 1.5	8.6 ± 4.0				r	35
		31.8	6.6	32.6	14.77	C$_6$H$_6$	2 p	gg
p-tolyl, H$_2$	65	34.0 ± 1.6	4.8 ± 3.8	34.8 ± 1.6	14.44 ± 0.82	Ph$_2$O	7 p, r	23
p-fluorophenyl, Me, H	66	35.0 ± 1.4	15.0 ± 3.7	35.8 ± 1.4	16.59 ± 0.80	p-cymene	3 p, r	24
m-chlorophenyl, Me, H	67	29.2	0.1	30.0	13.375	p-cymene	2 p	24
p-chlorophenyl, Me, H	68	32.0 ± 0.7	8.2 ± 2.0	32.8 ± 0.8	15.11 ± 0.44	p-cymene	3 p, r	24
p-anisyl, Me, H	69	34.2 ± 0.6	5.7 ± 1.4	35.0 ± 0.6	14.63 ± 0.35	Ph$_2$O	7 p, r	23
c-(CH$_2$)$_5$, OAc	70	44.0 ± 0.2	14 ± 4			PhEt	5 p	aa
n-C$_5$H$_{11}$, Me, CN	71	$k = 1.63 \times 10^{-4}$ s⁻¹ at 80 °C				PhMe		39
Me$_3$CCH$_2$, Me, CN	72	$k = 1.58 \times 10^{-2}$ s⁻¹ at 80 °C				PhMe		39
	72a	$k = 1.36 \times 10^{-2}$ s⁻¹ at 80 °C				PhMe	diastereomer	39
c-(CH$_2$)$_6$, CN	73	26.6 ± 0.1	3.0 ± 0.1	27.2 ± 0.1	13.93 ± 0.02	PhMe	9 p, r	z
c-(CH$_2$)$_4$CH, Me, CN	74	$k = 1.30 \times 10^{-4}$ s⁻¹ at 80.5 °C				PhMe		ff
Me$_3$C, Et$_2$	75	$k = 1.09 \times 10^{-2}$ s⁻¹ at 180 °C				PhEt		45
(i-C$_3$H$_7$)$_2$, Et	76	$k = 6.99 \times 10^{-3}$ s⁻¹ at 180 °C				PhEt		45
c-(CH$_2$)$_7$, Me	77	34.8	9	35.8 ± 1.0	15.38 ± 0.52	C$_6$H$_6$	3 p	30
c-(CH$_2$)$_4$, i-C$_3$H$_7$CH$_2$	78	37.7 ± 0.1	11 ± 0			PhEt	3 p	aa
c-(CH$_2$)$_4$, Me$_3$C	79	32.9 ± 1.1	6 ± 3			PhEt	3 p	aa
1-bicyclo[3.2.2]nonyl	80	42.1 ± 0.6	10.3 ± 1.2	43.1 ± 0.6	15.68 ± 0.26	C$_6$H$_6$	3 p, r	47
1-bicyclo[3.3.1]nonyl	81	$k = 6.88 \times 10^{-4}$ s⁻¹ at 300 °C				C$_6$H$_6$		47
2-(2-endo-methylbicyclo[2.2.2]octyl)	82	$k = 2.43 \times 10^{-3}$ s⁻¹ at 200 °C				C$_6$H$_6$		ee
3-noradamantyl	83	57.0 ± 0.4	14.8 ± 0.7	58.2 ± 0.4	16.79 ± 0.15	C$_6$H$_6$	4 p, r	47
Ph, Et, H	84	32.2	7.6	32.2	14.20		2 p	gg
p-tolyl, Me, H	85	30.2	2.3	30.8	13.83	p-cymene	2 p	24
o-anisyl, Me, H	86	31.6 ± 0.1	7.8 ± 0.6	32.4 ± 0.02	15.02 ± 0.02	p-cymene	3 p, r	24
m-anisyl, Me, H	87	40.9	30.3	41.7	19.94	p-cymene	2 p, r	24
p-anisyl, Me, H	88	30.2	2.8	31.0	13.93	p-cymene	2 p, r	24
Ph, MeOCH$_2$, H	89		7.4 ± 0.6	34.0 ± 0.1		PhEt	6 p	hh
m-CF$_3$C$_6$H$_4$, Me, H	90	32.2	8.4	33.0	15.15	p-cymene	2 p, r	24
Ph, Me$_2$	91	29.0 ± 0.3	11.3 ± 0.3	29.8 ± 0.15	15.74 ± 0.19	PhMe	9 p, r	28
		29.6 ± 1.3	12.5 ± 4.0	30.2 ± 1.3	16.00 ± 0.89	PhMe	8 p, r	ii
		28.8 ± 0.1	10.4 ± 0.3	29.4 ± 0.1	15.54 ± 0.06	PhEt	3 p, r	64
p-FC$_6$H$_4$, Me$_2$	92	28.2 ± 1.2	8.7 ± 3.6	28.8 ± 1.2	15.15 ± 0.81	PhMe	r	jj
p-ClC$_6$H$_4$, Me$_2$	93	27.2 ± 0.4	6.5 ± 1.3	27.8 ± 0.4	14.68 ± 0.29	PhMe	r	jj
m-ClC$_6$H$_4$, Me$_2$	94	27.6 ± 0.6	7.8 ± 2.0	28.2 ± 0.6	14.95 ± 0.41	PhMe	r	jj
p-BrC$_6$H$_4$, Me$_2$	95	28.0 ± 0.2	4.5 ± 0.7	28.6 ± 0.2	15.21 ± 0.15	PhMe	4 p, r	ii
PhO, Me$_2$	96	32.3 ± 0.5	−2.5 ± 2	33.2 ± 0.5		tetralin		kk
PhS, Me$_2$	97	24.9 ± 0.5	−12.6 ± 2	25.7 ± 0.5		tetralin		kk
Ph, c-(CH$_2$)$_2$	98	31.6 ±1.6	−5.5 ± 3.6	32.4 ± 1.6	12.20 ± 0.77	C$_6$H$_6$, PhEt	cf. II.A.1, r	31
Ph, Me, CN	99			20.2	12.28	C$_6$H$_6$	nrd	x
c-(CH$_2$)$_7$, CN	100	23.0 ± 1.3	−3.7 ± 4.2	23.6 ± 1.3	12.5 ± 4.2	PhMe	9 p, r error	z
c-(CH$_2$)$_5$CH, Me, CN	101	$k = 2.27 \times 10^{-4}$ s⁻¹ at 80.5 °C				PhMe		ff
Me$_3$CCH$_2$, Et$_2$	102	$k = 3.72 \times 10^{-2}$ s⁻¹ at 180 °C				PhEt		45
Me$_3$CCH$_2$, Me$_2$CH, Me	103	$k = 4.62 \times 10^{-2}$ s⁻¹ at 180 °C				PhEt		45

TABLE I (Continued)

R_1, R_2, R_3	compd	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	E_a, kcal mol^{-1}	log A	solvent	notes	ref
$(Me_2CH)_3$	104	$k = 2.10 \times 10^{-2}$ s^{-1} at 180 °C				PhEt		45
c-$(CH_2)_5$, Me_2CHCH_2	105	41.4 ± 0.7	16 ± 2			PhEt	3 p	aa
c-$(CH_2)_5$, Me_3C	106	37.8 ± 0.3	14 ± 1			PhEt	3 p	aa
[c-$(CH_2)CH]_2$, Me_2CH	107	38.0 ± 0.2	17.6 ± 0.5	38.7 ± 0.2	17.20 ± 0.11	Ph_2O-iq	7 p, r	s
[c-$(CH_2)CH]_3$	108	34.2 ± 0.3	12.8 ± 0.7	35.0 ± 0.3	16.13 ± 0.16	Ph_2O-iq	13 p, r	s
trans-9-decalyl	109	41.8 ± 0.3	15.9 ± 0.6			PhEt	3 p	ll
cis-9-decalyl	109a	41.8 ± 0.1	15.4 ± 0.3			PhEt	3 p	ll
2-camphyl	110		7.2	43.9	14.63	hexadecane	3 p	mm
1-bicyclo[3.3.2]decyl	111	41.5 ± 0.2	15.9 ± 0.4	43.3 ± 0.2	16.89 ± 0.10	C_6H_6	4 p, r	47
1-adamantyl	112	60.6 ± 2.6	31.5 ± 4.8	61.8 ± 2.6	20.38 ± 1.04	C_6H_6	4 p, r	58
twistyl	113	$k = 4.6 \times 10^{-5}$ s^{-1} at 300 °C				C_6H_6		47
Ph, n-C_3H_7, H	114		8.5 ± 1.0	35.5 ± 0.4				hh
p-EtC_6H_4, Me, H	115	29.8	1.6	30.6	13.66	p-cymene	2 p, r	24
$PhCH_2$, Me_2	116	35.6 ± 0.5	4.1 ± 2	36.4 ± 0.5		tetralin		kk
		46.5 ± 1.2	27.1 ± 2.3			Ph_2O	6 p	25
p-MeC_6H_4, Me_2	117	26.2 ± 2.5	2.7 ± 7.3	26.8 ± 2.5	13.84 ± 0.60	PhMe	3 p	jj
		28.6 ± 0.7	10.3 ± 2.2	29.3 ± 0.7	15.52 ± 0.49	PhMe	6 p, r	ii
Ph, Et, Me	118	27.3 ± 0.8	6 ± 3			PhMe	5 p	nn
Ph, c-$(CH_2)_3$	119	29.2 ± 0.8	4.9 ± 2.2	30.0 ± 0.8	14.38 ± 0.49	PhEt	5 p, r	31
[$Me_2CHCH_2]_2$, CN	120	$k = 4.95 \times 10^{-5}$ s^{-1} at 80 °C				PhMe		39
$PhCH_2$, Me, CN	121	$k = 1.16 \times 10^{-4}$ s^{-1} at 80 °C				PhMe		oo
p-$ClC_6H_4CH_2$, Me, CN	122	$k = 8.8 \times 10^{-5}$ s^{-1} at 80 °C				PhMe		oo
p-$O_2NC_6H_4CH_2$, Me, CN	123	$k = 1.00 \times 10^{-4}$ s^{-1} at 80 °C				PhMe		oo
PhCO, Me_2	124	30.0 ± 1.2	11.1 ± 3.5			cumene	3 p	pp
n-C_8H_{17}, Me_2	125	$k = 2.35 \times 10^{-4}$ s^{-1} at 180 °C				PhEt		45
$(n$-$C_4H_9)_2$, Et	126	$k = 7.40 \times 10^{-4}$ s^{-1} at 180 °C				PhEt		45
c-$(CH_2)_6$, Me_3C	127	35.0 ± 1.2	15 ± 3			PhEt	3 p	aa
c-$(CH_2)_6$, Me_2CHCH_2	128	34.2 ± 1.0	7 ± 2			PhEt	3 p	aa
1-homoadamantyl	129	47.1 ± 1.3	13.8 ± 2.6	48.1 ± 1.3	16.47 ± 0.56	C_6H_6	4 p, r	47
3-homoadamantyl	130	43.5 ± 1.9	18.1 ± 4.2	44.5 ± 1.9	17.37 ± 0.91	C_6H_6	4 p, r	47
p-EtC_6H_4, Me_2	131	30.2 ± 0.7	14.7 ± 0.7	30.8 ± 0.7	16.47 ± 0.5	PhMe	3 p, r	ii
$Ph(CH_2)_2$, Me_2	132	32.6	9.3	33.4	15.36	PhEt	2 p	gg
Ph, Me_2CH, Me	133	27.1	5			PhEt		46
		28.8	10					nn
$PhCMe_2$, Me, H	134	$k = 1.33 \times 10^{-3}$ s^{-1} at 254 °C				Ph_2O		qq
Ph, c-$(CH_2)_4$	135	24.6 ± 0.3	6.7 ± 1.1	25.2 ± 0.3	14.72 ± 0.24	C_6H_6	6 p, r	31
PhO, c-$(CH_2)_4$	136	36.1 ± 1.0	5 ± 2			PhEt	4 p	aa
c-$(CH_2)_9$, CN	137	27.0 ± 0.9	5.4 ± 2.8	27.8 ± 1.0	14.45 ± 0.63	PhMe	6 p, r	z
$(n$-$C_4H_9)_2$, Me_2CH	138	$k = 1.47 \times 10^{-3}$ s^{-1} at 180 °C				PhEt		45
$(Me_3CCH_2)_2$, Me	139	30.0 ± 0.5	5.2 ± 1.2			Ph_2O	6 p	43
Ph, c-$(CH_2)_5$	140	30.0 ± 0.8	14.3 ± 2.2	30.6 ± 0.7	16.39 ± 0.47	C_6H_6	5 p, r	31
p-$Me_2CHC_6H_4$, Me_2	141	30.4 ± 0.6	14.9 ± 2.0	31.0 ± 0.6	16.52 ± 0.43	PhMe	4 p, r	ii
2-(1,2-dimethyladamantyl)	142	41.6 ± 0.1	15 ± 0			PhEt	3 p	aa
p-Ph-C_6H_4, H_2	143	32.0 ± 0.9	1.3 ± 0.2	32.8 ± 0.9	13.66 ± 0.46	Ph_2O	6 p, r	23
Ph_2, H	144	26.0	2.3	26.6	13.78	PhMe	2 p	rr
p-$MeOC_6H_4CMe_2$, Me, H	145	$k = 1.35 \times 10^{-3}$ s^{-1} at 256 °C				Ph_2O		qq
PhO, c-$(CH_2)_5$	146	36.3 ± 0.5	3 ± 1			PhEt	4 p	aa
$(n$-$C_4H_9)_2$, Me_3C	147	$k = 1.09 \times 10^{-2}$ s^{-1} at 180 °C				PhEt		45
c-$(CH_2)_6$, Ph	148	23.4 ± 0.7	5.1 ± 2.4	24.0 ± 0.7	14.36 ± 0.51	C_6H_6	7 p, r	31
p-MeC_6H_4, c-$(CH_2)_5$	149	25.2 ± 0.5	−0.4 ± 1.7	25.8 ± 0.6	13.18 ± 0.38		3 p, r	jj
$PhCMe_2CH_2$, Me_2	150	35.2 ± 0.1	11.6 ± 0.1	36.0 ± 0.1	15.90 ± 0.0	PhMe	4 p, r	t
p-$Me_3CC_6H_4$, Me_2	151	30.0 ± 1.2	13.7 ± 3.7	30.6 ± 1.2	16.26 ± 0.81	PhMe	3 p, r	ii
Ph, $(Me_2CH)_2$	152	27.1 ± 1.1	6.1 ± 3.3			PhEt	3 p, r	46
2-(endo-2-Ph-norbornyl)	153	$k = 2.91 \times 10^{-2}$ s^{-1} at 60 °C						59
2-(exo-2-Ph-norbornyl)	154	$k = 6.2 \times 10^{-5}$ s^{-1} at 60 °C						59
p-$MeCONHC_6H_4CMe_2$, Et	155	$k = 2.24 \times 10^{-3}$ s^{-1} at 256 °C				Ph_2O		qq
$PhCMe_2CH_2$, Me, CN	156		22.8		12.28		nrd	x
$PhCH_2$, Ph, H (meso)	157	32.4 ± 0.2	7.8 ± 0.4	33.2 ± 0.2	15.04 ± 0.09	PhEt	3 p, r	ss
$PhCH_2$, Ph, H (dl)	158	32.4 ± 0.1	8.2 ± 0.3	33.2 ± 0.1	15.12 ± 0.06	PhEt	3 p, r	ss
Ph, $(n$-$C_4H_9)_2$	159	27.0 ± 1.2	5.4 ± 3.8	27.7 ± 1.2	14.46 ± 0.81	PhEt	3 p, r	46
$EtPhCHCH_2$, Ph, H	160	$k = 5.6 \times 10^{-4}$ s^{-1} at 118.8 °C				xylene		tt
Ph_2MeCCH_2, Me_2	161	34.2 ± 0.1	11.0 ± 0.2	35.0 ± 0.1	15.75 ± 0.23	PhMe	4 p, r	t

[a] Abbreviations: nrd = no raw kinetic data provided, r = literature kinetic data recalculated by the author, p = number of rate-temperature points given, g = gas phase, iq = isoquinoline. Note: Most compounds in this table are named by specifying the groups R_1, R_2, R_3 attached to the α carbon. Since this system is awkward for azobicycloalkanes, such compounds are named directly; e.g., 42 is azo-1-norbornane.
[b] Steel, C.; Trotman-Dickenson, A. F. J. Chem. Soc. 1959, 975. [c] Forst, W.; Rice, O. K. Can. J. Chem. 1963, 41, 562. [d] Ramsperger, H. C. J. Am. Chem. Soc. 1927, 49, 912. Data recalculated by Kassel in ref f. [e] Taylor, H. A.; Jahn, F. P. J. Chem. Phys. 1939, 7, 470. [f] Rice, O. K.; Sickman, D. V. Ibid. 1936, 4, 242. [g] Leventhal, E.; Simonds, C. R.; Steel, C. Can. J. Chem. 1962, 40, 930. [h] Clark, D.; Pritchard, H. O. J. Chem. Soc. 1956, 2136. [i] Sandhu, H. S. J. Phys. Chem. 1968, 72, 1857. [j] Clark, W. D.; Swinehart, D. F.; McCoy, R. D. 132nd ACS meeting, New York, 1957, p 47S. [k] Martin, G.; Maccoll, A. J. Chem. Soc., Perkin Trans. 2 1977, 1887. [l] Timberlake, J. W., unpublished results. [m] Geiseler, G.; Hoffmann, J. Z. Phys. Chem. 1968, 57, 318. [n] Ramsperger, H. C. J. Am. Chem. Soc. 1928, 50, 714. [o] Wheatley, T. A. Diss. Abstr. 1961, 21, 3652. [p] Frankel, M. D.; Klager, K. J. Am. Chem. Soc. 1957, 79, 2953. [q] Blackham, A. U.; Eatough, N. L. Ibid. 1962, 84, 2922. [r] Levy, J. B.; Copeland, B. K. W. Ibid. 1960, 82, 5314. [s] Martin, J. C.; Timberlake, J. W. Ibid. 1970, 92, 978. [t] Prochazka, M. Collect. Czech. Chem. Commun. 1976, 41, 1557. [u] Lewis, F. M.; Matheson, M. S., J. Am. Chem. Soc. 1949, 71, 747. [v] Bawn, C. E. H.; Mellish, S. F. Trans. Faraday Soc. 1951, 47, 1216. [w] Petersen, R. C.; Markgraf, J. H.; Ross, S. D. J. Am. Chem. Soc. 1961, 83, 3819. [x] Lim,

TABLE I (Continued)

D.; Collect. Czech. Chem. Commun. 1968, 33, 1122. [y] Overberger, C. G.; O'Shaughnessy, M. T.; Shalit, H. J. Am. Chem. Soc. 1949, 71, 2661. [z] Overberger, C. G.; Biletch, H.; Finestone, A. B.; Lilker, J.; Herbert, J. J. Am. Chem. Soc. 1953, 75, 2078. [aa] Giac, N. T., Inaugural Dissertation, University of Freiburg, 1977. [bb] Overberger, C. G.; Berenbaum, M. B. J. Am. Chem. Soc. 1951, 73, 2618. [cc] Hammond, G. S.; Neuman, R. C. Ibid. 1963, 85, 1501. [dd] Hammond, G. S.; Fox, J. R. Ibid. 1964, 86, 1918. [ee] Hinz, J., Inaugural Dissertation, University of Freiburg, 1971. [ff] Overberger, C. G.; Lebovits, A. J. Am. Chem. Soc. 1954, 76, 2722. [gg] Cohen, S. G.; Groszos, S. J.; Sparrow, D. B. Ibid. 1950, 72, 3947. [hh] Scheppele, S. E.; Rapp, W. H.; Miller, D. W.; Wright. D.; Marriot, T. Ibid. 1972, 94, 539. [ii] Shelton, J. R.; Liang, C. K.; Kovacic, P. Ibid. 1968, 90, 354. [jj] Kovacic, P.; Flynn, R. R.; Gormish, J. F.; Kappelman, A. H.; Shelton, J. R. J. Org. Chem. 1969, 34, 3312. [kk] Ohno, A.; Ohnishi, Y. Tetrahedron Lett. 1969, 4405. [ll] Giac, N. T.; Rüchardt, Ch. Chem. Ber. 1977, 110, 1095. [mm] Berson, J. A.; Olsen, C. L.; Walis, J. S. J. Am. Chem. Soc. 1962, 84, 3337. [nn] McBride, J. M., Ph.D. Thesis, Harvard University, 1966. [oo] Overberger, C. G.; Biletch, H. J. Am. Chem. Soc. 1951, 73, 4880. [pp] Zawalski, R. C.; Lisiak, M.; Kovacic, P.; Luedtke, A.; Timberlake, J. W. Tetrahedron Lett. in press. [qq] Overberger, C. G.; Gainer, H. J. Am. Chem. Soc. 1958, 80, 4561. [rr] Cohen, S. G.; Wang, C. H. Ibid. 1955, 77, 2457. [ss] Scheppele, S. E.; Seltzer, S. Ibid. 1968, 90, 358. [tt] Overberger, C. G.; Finestone, A. B. Ibid. 1956, 78, 1638.

samples.[88] However, since most other methylenimines form cyclic trimers,[89] the structure of these crystals probably bears investigation.

cis-Azoisopropane, AIP(c), has also been well characterized;[90] in fact, it can be prepared quite easily in 95% purity by a nonphotochemical route.[91] As seen in Tables I and V, AIP(c)

AIP(c)
26%

AIP(t)
41%
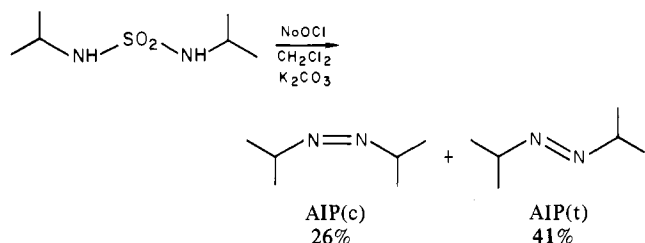
is less stable thermally than the trans isomer, but its half-life is still 10 min at 162 °C. Heating this compound leads to both decomposition and reversion to trans, the relative importance of these reactions depending on temperature.[92] Neither isomer is easily dealt with, however, because of tautomerization at the decomposition temperature.[62,93,94]

An important discovery about cis-azoalkanes was published in 1969 by Mill and Stringham.[95] These workers found that irradiation of trans-azo-2-methyl-2-propane, ATB(t), at low temperatures resulted in isomerization to the bright yellow cis isomer which lost nitrogen upon warming. Thus ATB(c) differs

ATB(t)

ATB(c)

$$2 \quad \dot{Y} \quad + \quad N_2$$
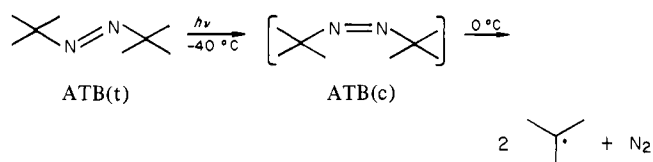
drastically from AIP(c) which has the same half-life at a temperature 173 °C higher! (Cf. Table V.) Further work showed that irradiation of most acyclic azoalkanes at sufficiently low temperature would generate the cis isomer.[27,95,96] The most labile example seen to date is **17c**, which was produced by

17c
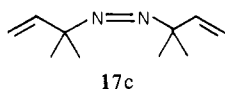
irradiation of **17t** in a matrix at -150 °C but which disappeared on warming to -120 °C.[27] For the somewhat more stable cis azo compounds, it has been possible to obtain accurate rate constants and activation parameters for their disappearance; these results are included in Table V. The fact that many cis azo compounds undergo thermolysis at low temperatures is of potential utility in free-radical-initiated polymerization.

In order to rationalize the known data on stability of various cis azo compounds, one must consider the same two factors which are important for the trans isomers: incipient radical stability and steric bulk of the attached R groups. The difference between **17c** and ATB(c), for example, is surely due to the greater stability of α,α-dimethylallyl radical than tert-butyl rad-

ical[20,21] whereas the difference between AIP(c) and ATB(c) must be primarily of steric origin. It is particularly instructive to compare cis-azoalkanes with their trans isomers, using appropriate olefins as models to estimate the steric strain.[27] $\Delta G^{\ddagger}(298 \, °C)$ for thermolysis of ATB(t) is 37.4 kcal mol^{-1}, whereas $\Delta H^{\ddagger}(298 \, °C)$ for the cis compound is only 18.7 kcal mol^{-1}. The difference between these figures, 18.7 kcal mol^{-1}, must be due in part to the steric strain of ATB(c), estimated to be 10.5 kcal mol^{-1} from the known strain of cis-di-tert-butylethylene.[101] Thus steric strain fails to account for 8.2 kcal mol^{-1} of the $\Delta G^{\ddagger}$ difference between cis- and trans-ATBs. When applied to other cis-trans pairs, the same reasoning gives a remarkably constant value of 7–8 kcal mol^{-1} for the "inherent" cis-trans difference. This difference arises from the higher ground-state energy of cis relative to trans azo compounds (see below).

Rüchardt and co-workers[96] have studied the effect of ring size on thermolysis rates of cis-1-methylazocycloalkanes. Since homolysis of these compounds should be about 20 kcal mol^{-1} less endothermic than in the trans isomers, the Hammond postulate would predict less C–N bond stretching in the transition state. Thus the ring size effect, which was considerable in trans-azoalkanes (Figure 2), should be reduced in the cis isomers. Instead, log k_{rel} was found to be strongly dependent on ring size, as reflected in the monotonic decrease of decomposition temperature seen in Table V. The fact that the five-membered ring was not merely equal in rate to the six-membered ring, but was actually slower, means that the above explanation is insufficient; the five-ring ground state must be of lower energy than the six-ring. Some support for this idea is found in the considerably shorter wavelength absorption maximum of the five-ring compound than the other compounds (see section III). The large rate enhancement observed for the seven- and eight-membered rings was quite reasonably attributed to steric acceleration by increasingly bulky cis alkyl groups (F strain).[76]

For most of the compounds listed in Table V, heating leads to nitrogen and free radicals. If the radical to be formed were of high energy, however, one might expect that a cis-azoalkane could be found which would isomerize to the trans-azoalkane instead of decomposing. Azo-1-norbornane (**42c**) is just such

42c
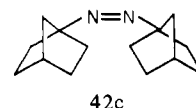
a case (cf. Figure 3); in fact, the activation enthalpy for isomerization is sufficiently high that **42c** is isolable as stable yellow crystals. Even greater stability has been found for the next lower homologue, azo-1-bicyclo[2.1.1]hexane, whose half-life for isomerization to the trans isomer is 10 min at 139.5 °C.[98] Since tautomerization is impossible, these compounds are probably the most conveniently studied acyclic cis-azoalkanes yet prepared. For example, differential scanning calorimetry provided the first direct measurement of the cis–trans energy difference (12.6 kcal mol^{-1} for **42c** → **42t**). Under the assumption that

TABLE II; Activation Parameters for Thermolysis of Unsymmetrical *trans*-Azoalkanes $(R_1N=NR_2)^a$

R_1	R_2	compd	$\Delta H^{\ddagger}$, kcal mol⁻²	$\Delta S^{\ddagger}$, eu	E_a	log A	solvent	notes	ref
Me	Me₂CH	177			47.5		g		61
Me	H₂C=CHCH₂	178		5.3 ± 1.5	35.4 ± 0.7	14.51 ± 0.32	g	4 p	65
Me	H₂C=CHCMe₂	179	35.3 ± 1.0	13.6 ± 2.4	36.2 ± 1.0	16.32 ± 0.53	p-DIPB	5 p, r	27
Me	PhCHMe	180	38.0 ± 1.8	10.4 ± 4.1	38.9 ± 1.8	15.67 ± 0.90	Ph₂O-iq	4 p, r	b
Et	Me₂CH	181	48.3 ± 1.1	14.0 ± 1.9	49.5 ± 1.1	16.6 ± 0.4	g	toluene carrier, r	c
H₂C=CHCH₂	n-C₃H₇	182		6.6 ± 1.3	35.6 ± 0.5	14.80 ± 0.28	g	NO inhibitor 3 p	65
H₂C=CHCH₂	Me₃C	183		−2.8 ± 1.3	29.8 ± 0.3	12.73 ± 0.26	g	NO inhibitor 4 p	65
Me₂CH	H₂C=CHCMe₂	184	32.8 ± 0.3	11.7 ± 0.8	33.6 ± 0.3	15.90 ± 0.18	p-DIPB	5 p, r	27
Me₂CH	PhCHMe	185	35.6 ± 0.1	9.0 ± 0.1	36.4 ± 0.1	15.35 ± 0.03	Ph₂O	3 p, r	d
Me₂CH	PhCMe₂	186	35.8 ± 0.2	13.7 ± 0.5	36.6 ± 0.2	16.35 ± 0.12	Ph₂O	4 p, r	d
EtOOC	Me₂CCN	187	32.2 ± 1.3	1.7 ± 3.0	33.0 ± 1.3	14.08 ± 0.69	decalin	4 p, r	e
O₂NCMe₂	p-BrC₆H₄	188	31.5 ± 1.0	1.6 ± 2.4	32.4 ± 0.9	13.72 ± 0.51	o-C₆H₄Cl₂	4 p, r, rcs	f
Me₃C	Me₂CCN	189	34.0 ± 0.4	14.7 ± 1.1	34.8 ± 0.4	16.53 ± 0.25	hexadecane	5 p, r	g
Me₃C	H₂C=CHCMe₂	190	26.8 ± 0.2	−0.1 ± 0.6	27.6 ± 0.2	13.28 ± 0.13	p-DIPB	5 p, r	27
Me₃C	Ph	191	$k = 1.06 \times 10^{-3}$ s⁻¹ at 300 °C				C₆H₆		64
Me₃C	1-norbornyl	192	48.3 ± 0.2	14.8 ± 0.4	49.5 ± 0.2	16.73 ± 0.09	C₆H₆	3 p, r	47
Me₃C	Me₃CCH₂CMeCN	193	29.4 ± 0.2	9.2 ± 0.6	30.2 ± 0.2	15.29 ± 0.14	decalin	3 p, r	g
Me₃C	1-bicyclo-[2.2.2]octyl	194	46.5 ± 0.2	14.9 ± 0.4	47.5 ± 0.2	16.73 ± 0.09	C₆H₆	3 p, r	47
Me₃C	Me₃CH₂CMe₂	195	38.1 ± 0.6	12.3 ± 1.3			Ph₂O	6 p	43
Me₂C	1-adamantyl	196	44.9 ± 1.0	13.6 ± 2.2	45.9 ± 1.1	16.45 ± 0.43	C₆H₆	3 p, r	47
Me₃C	(Me₃CCH₂)₂CMe	197	33.8 ± 0.6	5.7 ± 1.4			Ph₂O	6 p	43
NCCMe₂	MeOCMe₂	198	31.4 ± 1.0	14.8 ± 3.0	32.1 ± 1.0	16.5 ± 1.0	decalin	ose	h
NCCMe₂	Ph	199	42.1 ± 1.3	18.5 ± 3.0	43.1 ± 1.3 41.1	17.43 ± 0.65	decalin	4 p, r, rcs nrd, rcs	e i
NCCMe₂	1-adamantyl	200	33.4 ± 0.7	8.7 ± 1.8	34.2 ± 0.7	15.25 ± 0.39	C₆H₆	4 p, r	g
MeC(CN)₂	p-MeOC₆H₄	201	33.2	14.6	33.9 27.7	12.75	decane o-C₆H₄Cl₂	nrd, ose 7 p	j k
MeC(CN)₂	2,6-diMeC₆H₃	202			31.2	17.31	o-C₆H₄Cl₂	5 p	k
Et₂CH	PhCEt₂	203	38.3 ± 0.4	19.3 ± 1.1	38.9 ± 0.4	17.57 ± 0.24	Ph₂O	5 p, r	d
Ph	c-(CH₂)₄CMe	204	51.3 ± 4.0	16.3 ± 7.2	52.5 ± 4.0	17.1 ± 1.6	C₆H₆	3 p, r	30
Ph	c-(CH₂)₅CMe	205	51.5	16			C₆H₆	nrd	30
Ph	PhCMeCN	206	31.8 ± 0.4	13.3 ± 1.1	32.4 ± 0.4	16.22 ± 0.23	decalin	4 p, r	e
Ph	CMe₂CH₂-CMeCN	207	37.0 ± 1.6	12.8 ± 3.8	37.8 ± 1.6	16.17 ± 0.84	decalin	4 p, r	e
c-(CH₂)₅CH	PhCMe₂	208	$k = 2.0 \times 10^{-6}$ s⁻¹ at 90 °C				cumene		l
c-(CH₂)₄CMe	PhCMe₂	209	32.0 ± 0.7	8.9 ± 1.8	32.2 ± 0.6	15.20 ± 0.37	PhCMe₃	3 p, r	30
EtMeCCHMe	EtMeCCPhMe	210	34.6 ± 0.9	14.7 ± 2.4	35.4 ± 0.9	16.55 ± 0.53	Ph₂O	4 p, r	d
c-(CH₂)₅CMe	PhCMe₂	211	31.4 ± 2.2	8.0 ± 5.8	32.0 ± 2.2	15.10 ± 1.25	PhCMe₃	3 p, r	30
PhCH₂	PhCMe₂	212	36.0	12.0	36.8	16.09	cumene	2 p, r	74
o-MeC₆H₄	PhCMe₂CH₂-CMeCN	213	40.5 ± 0.2	21.8 ± 0.6	41.3 ± 0.2	18.14 ± 0.12	decalin	4 p, r	e
1-norbornyl	*endo*-2-methyl-norbornyl	214	47.6	12			C₆H₆	nrd	64
1-norbornyl	*exo*-2-methyl-norbornyl	215	48.8	16			C₆H₆	nrd	64
1-norbornyl	1-bicyclo-[2.2.2]octyl	216	$k = 1.11 \times 10^{-5}$ s⁻¹ at 300 °C				C₆H₆		47
1-norbornyl	1-adamantyl	217	$k = 2.80 \times 10^{-5}$ s⁻¹ at 300 °C				C₆H₆		47
endo-2-methyl-norbornyl	PhCMe₂	218	32.8	9			PhCMe₃	nrd	64
exo-2-methyl-norbornyl	PhCMe₂	219	33.7	15			PhCMe₃	nrd	64
bicyclo[2.2.2]-octyl	1-adamantyl	220	$k = 2.51 \times 10^{-4}$ s⁻¹ at 300 °C				C₆H₆		47

^{a} Abbreviations: p-DIPB = p-diisopropylbenzene, rcs = related compounds studied, ose = other solvents employed. (See Table I for other abbreviations.) ^{b} Seltzer, S.; Dunne, F. T. *J. Am. Chem. Soc.* 1965, 87, 2628. ^{c} Martin, G.; Maccoll, A. *J. Chem. Soc., Perkin Trans. 2* 1977 1887. ^{d} Overberger, C. G.; DiGiulio, A. V. *J. Am. Chem. Soc.* 1959, 81, 2154. ^{e} Prochazka, M.; Ryba, O.; Linn, D. *Collect. Czech. Chem. Commun.*, 1971, 36, 3650. ^{f} Kerber, R.; Nuyken, O.; Weithmann, L. *Chem. Ber.* 1975, 108, 1533. ^{g} Prochazka, M.; Ryba, O.; Linn, D. *Collect. Czech. Chem. Commun.* 1971, 36, 2640. ^{h} Malament, D. S. *Isrl. J. Chem.* 1973, 11, 819. ^{i} Kerber, R.; Nuyken, O. *Makromol. Chem.* 1973, 164, 183. ^{j} Kerber, R.; Nuyken, O.; Steinhausen, R. *Ibid.* 1974, 175, 3225. ^{k} Kerber, R.; Nuyken, O.; Pasupathy, V. *Ibid.* 1973, 170, 155. ^{l} Neuman, R. C.; Alhadeff, E. S. *J. Org. Chem.* 1970, 35, 3401.

thermolysis of both isomers proceeds via the same transition state, one can construct a complete energy diagram (Figure 6) which shows why heating **42c** causes isomerization but no decomposition. *cis*-Azonorbornane is an energy-storing compound because irradiation converts the trans compound to the higher energy but stable cis isomer. Heating or addition of an appropriate catalyst could release the stored energy. In practice, azonorbornane is an expensive compound for such use, but

azobenzene is under study for solar energy storage.[102,103]

The behavior of **42c** contrasts sharply with that of ATB(c) which only decomposes to nitrogen. Although the cis–trans energy difference has not been determined for ATB,[104] one can construct an energy diagram, again assuming that cis and trans decompose via the same transition state (cf. Figure 7). Since isomerization is not observed, the transition state for this process must lie above that for homolysis. A quantitative treatment

TABLE III. Differences in Free Energy of Activation between Symmetrical and Unsymmetrical Azo Compounds

R$_1$	R$_2$	temp, °C	$\Delta\Delta G_1^{\ddagger,a}$ kcal mol^{-1}	$\Delta\Delta G_2^{\ddagger,b}$ kcal mol^{-1}	ref
Me	i-Pr	25	3.5	0.7	27
Me	α-phenethyl	25	13.7	3.8	27
i-Pr	α-phenethyl	25	10.2	3.1	27
i-Pr	cumyl	25	11.4	6.0	27
t-Bu	cumyl	25	8.4	3.3	27
Me	allyl	25	14.0	1.0	27
n-Pr	allyl	25	10.3	0.5	27
t-Bu	allyl	25	7.5	−2.4	27
Me	α,α-di-methyl-allyl	25	16.1	6.6	27
i-Pr	α,α-di-methyl-allyl	25	13.7	4.8	27
t-Bu	α,α-di-methyl-allyl	25	10.5	2.2	27
t-Bu	2-cyano-propyl	25	7.7	2.0	27
benzyl	α-phenethyl	25	0.7	2.2	27
2-methoxy-propyl	2-cyano-propyl	25	8.8	−1.2	66
t-Bu	tert-octyl	25	3.0	3.4	42
t-Bu	DNPE^d	25	5.3	3.7	43
1-methyl-cyclo-pentyl	cumyl	200	7.0	3.6	64
1-methyl-cyclo-hexyl	cumyl	200	7.9	3.7	64
endo-2MN^c	cumyl	200	9.7	4.4	64
exo-2MN^c	cumyl	200	7.4	2.7	64
1-norbornyl	endo-2MN^c	200	7.6	4.2	64
1-norbornyl	exo-2MN^c	200	8.5	7.3	64
1-norbornyl	1-bicyclo-[2.2.2]-octyl	300	0.4	2.2	47
1-norbornyl	1-adamantyl	300	1.5	3.5	47
1-bicyclo-[2.2.2]-octyl	1-adamantyl	300	4.0	1.0	47
1-norbornyl	t-Bu	300	7.9	6.0	47
1-bicyclo-[2.2.2]-octyl	t-Bu	300	7.1	5.0	47
1-adamantyl	t-Bu	300	5.4	4.3	47

^{a} Free-energy difference between azoalkane listed and its more stable symmetrical counterpart (R$_1$N=NR$_1$). ^{b} Free-energy difference between azoalkane listed and its less stable symmetrical counterpart (R$_2$N=NR$_2$). ^{c} 2MN = 2-methylnorbornyl; endo and exo indicate configuration of azo group. ^{d} α,α-Dineopentylethyl.

TABLE IV. Comparison of cis- and trans-Azomethanes[53]

property	trans	cis
UV λ$_{max}$, nm (ε), hexane	352 (25)	368 (240)
dipole moment, D	0	3.2^a
bp, °C	1.5	95
C—N=N bond angle, deg	111.9^a	119.4^a
C—N length, A	1.474^a	1.485^a
NMR chemical shift^b	3.76	3.62

^{a} By microwave spectroscopy.[54] ^{b} In parts per million downfield from Me$_4$Si.

showed that if less than 2.2% of cis-ATB goes to the trans isomer, $\Delta H^{\ddagger}$ for isomerization must lie at least 46.3 kcal mol^{-1} above ground-state trans-ATB.[105] Unfortunately, it is difficult to determine exactly how much cis goes to trans on account of the unfavorable ratio of extinction coefficients and the inaccuracy of nitrogen yields. Similar considerations[105] in the case 42c revealed that much of the nitrogen produced on thermolysis
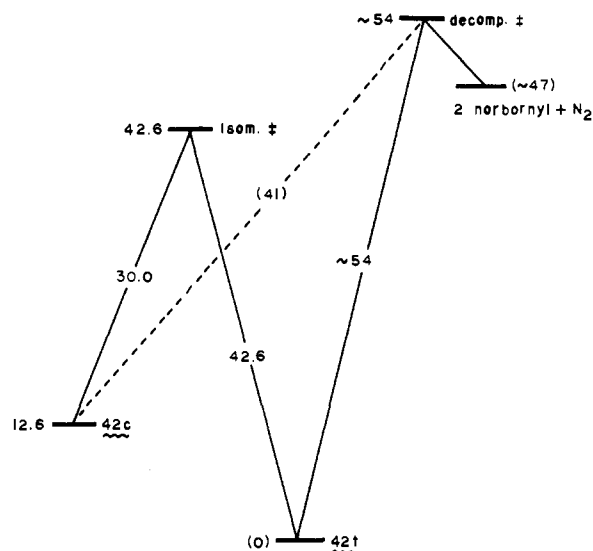
Figure 6. Enthalpy of 1-azonorbornane (42) and the transition states for isomerization and decomposition. Values in parentheses are assumed or calculated. Dashed line indicates a process not observed.
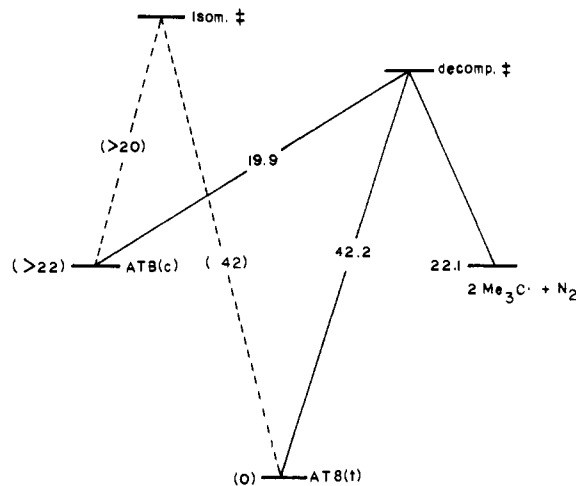
Figure 7. Enthalpy of azo-2-methyl-2-propane (ATB) and the transition states for isomerization and decomposition. See caption for Figure 6.

of trans arises by thermal isomerization to cis, followed by decomposition of cis.

It is clear from the above discussion that ATB(c) and 42c represent extreme cases; the former only decomposes and the latter only isomerizes. Interestingly, cis-azo-1-bicyclo[2.2.2]-octane (61c) and cis-azoadamantane (112c) undergo both re-

61c   112c
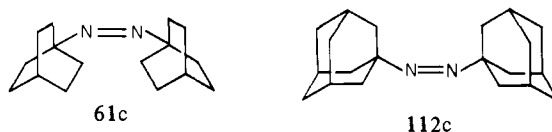
actions at once, implying that the transition states for decomposition and isomerization are of similar energy. Decomposition is favored by higher temperature and less polar solvent, but both processes are slowed by increasing the applied pressure.[106] Analysis of the product composition from 112c as a function of temperature allows one to extract activation parameters for each process. In hexane, for example, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 27.3 kcal mol^{-1} and 16.9 eu for decomposition and 23.8 kcal mol^{-1} and 4.3 eu for isomerization.[98]

Whereas thermolysis rates of trans-azoalkanes are unaffected by changes in solvent polarity, decomposition of ATB(c) is at least 50 times faster in pentane than in methanol.[97] The log

TABLE V. Data for cis-Azoalkanes $\left(\begin{array}{c} R \quad R' \\ N{=}N \end{array}\right)$

R, R^ra	λmax, nm (ε)	T, °C^b	ΔH‡, kcal mol^-1c	ΔS‡, eu	ref
i-Pr	382 (140)	162^d	39.9 ± 1.8	18.9 ± 4.1	92
t-Bu	447 (~100)	−11^d	19.9 ± 0.4	4.3 ± 1.5	27
			18.6 ± 1.0	5.6 ± 4.0	97
2-cyanopropyl	390	−60^e			27
tert-octyl	444	−70^e			27
cumyl	434	−100^e			27
α,α-dimethylallyl	442	−120^e			27
1-methylcyclopentyl	417	+9^f			96
1-methylcyclohexyl	450	−20^f			96
1-methylcycloheptyl	450	−43.5^f			96
1-methylcyclooctyl	450	−54.1^f			96
1-norbornyl	423 (88)	85.9^d	30.0 ± 0.5	11.2 ± 1.4	98
		100.5^d	31.8 ± 0.4	12.8 ± 1.2	99
		102.0^d	27.7 ± 0.7	1.6 ± 1.9	100
1-adamantyl	455 (93)	30.6^d	25.9 ± 0.5	13.4 ± 1.6	99
1-bicyclo[2.2.2]octyl	444 (78)	45.5^d	25.9 ± 0.3	9.3 ± 0.9	98
1-bicyclo[2.1.1]hexyl	404 (120)	139.5^d	30.3 ± 0.5	0.8 ± 1.3	98
CH3, α,α-dimethylallyl	380	7^d	23.1 ± 0.3	10.5 ± 1.1	27
i-Pr, α,α-dimethylallyl	385	−8^d	21.8 ± 0.4	10.5 ± 1.6	27
t-Bu, α,α-dimethylallyl	444	−110^e			27

a When the azoalkane is symmetrical, the R group is listed only once. b Temperature at which the half-life of cis-azoalkane is 10 min. c For disappearance of cis-azoalkane. d Calculated from activation parameters. e Approximate value in polymethylmethacrylate. f Calculated from data in ref 96, assuming ΔS‡ = 10 eu.

of the rate constant was found to be proportional to the solvent parameter E_T with a slope of −0.071. The effect of solvent on isomerization was then examined for 42c, giving a slope of −0.015 for the log k vs. E_T plot.[100] Thus decomposition is more strongly retarded by polar solvents than isomerization. When the two processes are allowed to compete as in azo-adamantane, polar solvents should diminish the importance of decomposition, in accord with the observed trend.

Schulz and Rüchardt[97] have attributed the strong solvent dependence of decomposition rate in part to expansion of the C—N=N angles during homolysis. Cyclic cis-azoalkanes show a similar solvent effect,[107] but of course these compounds cannot undergo significant angle expansion. Due to their high dipole moment (cf. Table IV), all cis-azoalkanes should be stabilized by polar solvents. The nonpolar nature of the products suggests that the transition state is less polar than the starting material, so the solvent effect is as expected. The reason why Rüchardt postulated angle expansion in the acyclic cases is that the exothermicity of their decomposition suggests an earlier transition state than the cyclic compounds and hence less change in dipole moment as the molecules surmount the activation barrier. In order for them to exhibit the same solvent effect as the cyclic compounds, some additional means of reducing the transition-state dipole moment was called for. The evidence for an earlier transition state in cis-azoalkanes is shaky, however, since the ring-size effect[96] on which this suggestion is based was over-shadowed by large changes in F strain (see above). The identical magnitude of substituent effects in cyclic azoalkanes and trans-azoalkanes was taken as evidence for a similar degree of bond breaking in the decomposition transition state of the two series.[107] The same reasoning can be used to compare cis and trans acyclic azo compounds; for example, the rate acceleration seen on replacing methyl by vinyl is the same in cis- and trans-ATB.[27] On the other hand, if vinyl is a larger group than methyl, steric acceleration of cis thermolysis may compensate for the lack of rate enhancement caused by an earlier transition state in this isomer.[100] Whereas one measure of steric size shows vinyl to be larger than methyl (and also larger than tert-butyl),[108] methyl exhibits a stronger preference for the equatorial position of cyclohexane than vinyl does.[109] Thus the evidence that thermolysis of cis-azoalkanes is characterized by an earlier transition state than that of the trans isomers is inconclusive. A recent theoretical calculation[110] on cis-diimide
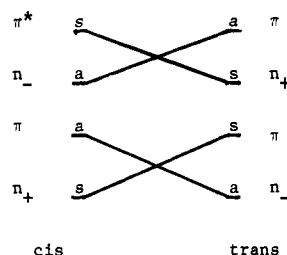
Figure 8. Orbital correlation diagram for diimide.

supports the idea of angle expansion during homolysis, but this cannot be a very strong requirement because cyclic azoalkanes decompose without particular difficulty (see below).

An alternate explanation of the solvent effect recognizes that more polar solvents have a higher internal pressure.[111] Since $\Delta V^{\ddagger}$ for loss of nitrogen is positive,[112] cis-azoalkanes should decompose more slowly in polar solvents. Of course this idea should also apply to the trans isomers, but these exhibit a negligible solvent dependence.[97,113] Cyclic azoalkanes containing α-cyano groups also show little solvent dependence because much of the solvation occurs at the polar substituent and is not lost in the transition state.[107] Although some details of cis-azoalkane homolysis remain obscure, the fact that most of these compounds decompose more slowly in polar solvents can be rationalized by their high dipole moment which decreases upon loss of nitrogen.

5. Mechanism of Isomerization

Three mechanisms for the thermal reversion of cis-azoalkanes to the trans isomers can be envisioned: (a) rotation about the N=N double bond, (b) inversion through one or both nitrogens, and (c) dissociation to diazenyl radicals and recombination. Experimental methods of distinguishing the first two possibilities do not readily come to mind; however, many theorists have tackled the problem.

Although the rotation mechanism is the only reasonable one for olefin isomerization, an orbital symmetry argument[114] suggests that azoalkanes do not follow this pathway. The MO diagram of cis- and trans-diimides is shown in Figure 8. Each MO is either symmetric (s) or antisymmetric (a) with respect to a C_2 axis which is maintained during rotation about the N=N
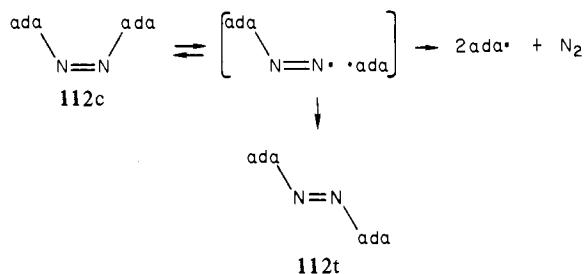
bond. Since the lowest three MO's are occupied in the ground state, this state of each isomer correlates with an excited state of the other isomer. Theoretical calculations on diimide and AM place the barrier to ground-state rotation in the range of 59–84 kcal mol⁻¹.[114-120] Rotation in the lowest excited state, on the other hand, is not expected to encounter such a barrier.

The inversion mechanism can involve a linear (**225**) or a semilinear (**226**) transition state, of which the former is much

$$R—N≡N—R \qquad \begin{array}{c} R\diagdown \\ N≡N—R \end{array}$$

$$225 \qquad\qquad 226$$
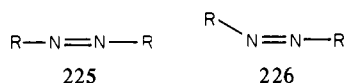
higher in energy[114,115] and can therefore be ruled out. Calculated values for the barrier to semilinearization of the trans isomer range from 37[120] to 66[117] kcal mol⁻¹. Since $\Delta H^{\ddagger}$ is 44 kcal mol⁻¹ for isomerization of **42t** (Figure 6) and about 40 kcal mol⁻¹ for that of AIP(t),[92] the lower end of the calculated range is more nearly correct. Moreover, thermal cis–trans isomerization probably occurs by semilinearization.

The third possible mechanism for azoalkane isomerization is one-bond homolysis and recombination of the diazenyl–alkyl pair. This possibility can be ruled out for **42c**, however, because the norbornyldiazenyl radical is known[70] to lose nitrogen, yet no nitrogen is detected during isomerization of **42c** to **42t**.[98] On the other hand, this mechanism does apply to certain phenyl-azoalkanes[67] and is not easily dismissed in the case of **112c** because this compound evolves nitrogen during isomerization.[98] Further work will be required to establish whether dissocia-tion–recombination is important for **112c**.

$$\begin{array}{c} ada \\ \diagdown \\ N≡N \\ / \\ ada \end{array} \quad \rightleftharpoons \quad \left[\begin{array}{c} ada \\ \diagdown \\ N≡N\cdot \quad \cdot ada \end{array} \right] \quad \longrightarrow \quad 2\,ada\cdot \; + \; N_2$$

$$\mathbf{112c}$$

$$\downarrow$$

$$\begin{array}{c} ada \\ \diagdown \\ N≡N \\ \diagdown \\ ada \end{array}$$

$$\mathbf{112t}$$

B. Thermochemistry

Recognizing that knowledge of the heat of formation (ΔH_f) of azoalkanes might be of use in understanding their decomposition, the author began a program in 1972 to determine some azoalkane ΔH_f's.[121] It was soon discovered[121] that ΔH_f for AIP,[122] the value on which all previous azoalkane thermochemical data were based, was in error by 11 kcal mol⁻¹. ΔH_f for azomethane, the simplest azoalkane, was shown[123] to be 35.5 kcal mol⁻¹, as compared with earlier estimates of 52[124] and 43.8[125a] kcal mol⁻¹. Thus thermolysis of AM to methyl radicals is more endothermic (32.5 kcal mol⁻¹) than was previously thought. The thermochemical data obtained are summarized in Table VI and the strain energies derived from these values are shown in Table VII. Some of the entries in Table VII are obtained by conventional group additivity methods[125a] while others come from force field parameterizations of the azo group.[126] The conclusions which can be drawn from these strain energies are discussed below.

The increase in ground-state energy of ATB upon replacement of the *tert*-butyl group by *tert*-octyl leads to a corresponding decrease in $\Delta H^{\ddagger}$ for thermolysis.[42] As shown above (Figure 5), this equality supports the two-bond homolysis mechanism. Even without steric repulsion, *cis*-azoalkanes lie higher in energy than their trans isomers by 6–8 kcal mol⁻¹. Unfortunately, a direct measurement of this "inherent" cis–trans energy difference, which is of fundamental importance in azo chemistry, is not yet available for a simple azoalkane; however, both ther-mochemical arguments[27] and theoretical calculations (Figure 9)
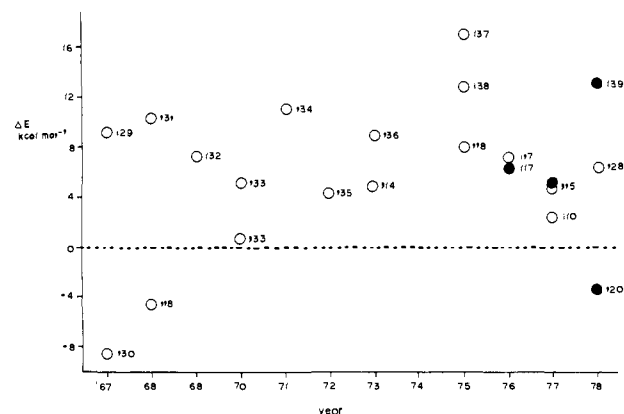
Figure 9. Results of theoretical calculations of the difference in ground state energy between *cis*- and *trans*-diimide (O) and azomethane (●). $\Delta E = E(\text{cis}) - E(\text{trans})$. Literature references are indicated next to each point.

support the 6–8-kcal mol⁻¹ value. Azo-1-norbornane (**42**), for which a direct measurement was possible,[98] gave a cis–trans difference of 12.6 kcal mol⁻¹ (cf. Figure 6). In this case, steric repulsion between bulky norbornyl groups is expected to contribute to the energy of the cis isomer. If it is true that ATB(c) lies above the trans isomer by 22 kcal mol⁻¹ (Figure 7), the effective size of a *tert*-butyl group must be substantially larger than that of 1-norbornyl in which the interfering carbons are "tied back". An X-ray structure of *cis*-azo-1-norbornane would be of interest, as would be determination of the cis–trans energy difference for other compounds in Table V. The higher energy of *cis*-azoalkanes than of the trans isomers accounts for their more rapid tautomerization and undoubtedly contributes to the faster rate with which *cis*-α-hydroxyazoalkanes undergo base-induced cleavage.[125b]

Tetramethyldiazetine exhibits ring strain comparable to that of other four-membered compounds (cyclobutane, 26.2;[125a] cyclobutene, 29.8;[125a] tetramethyldioxetane, 30.5 kcal mol⁻¹).[140] In contrast to the results for olefins however, six-membered azoalkanes (e.g., **230**) are more strained than five-membered ones (e.g., **229**). This surprising difference seems to arise from the smaller N=N—C bond angles in **229** which lead to less lone-pair repulsion than in **230**.[127] The fact that both five- and six-membered azoalkanes are more strained than their acyclic counterparts may account for the facile tautomerization observed in many cyclic azoalkanes which bear α hydrogens.[93,141-144] Furthermore, it will be shown below that ring strain can influence the propensity of azoalkanes to lose nitrogen.

Before leaving Table VII, one should note the prediction that the ring strain induced by a trans double bond in an eight-membered azoalkane (**234t**) nearly equals the higher energy of a cis azo group in **234c**.[126a] On the other hand, two different force-field calculations[126] make opposite predictions regarding the effect of α-methyl groups on azoalkane strain energy (cf. II.C.3.a). Comparison of bicyclic azoalkanes with the analogous olefins is not especially enlightening on account of the widely discrepant strain energies reported for norbornene (17.6,[145] 23.6,[146] 27.2[147] kcal mol⁻¹) and bicyclo[2.2.2]octene (11.3,[148] 16.0[146] kcal mol⁻¹).

C. Cyclic Azoalkanes

It will be noted from Table VIII that the stability of cyclic azoalkanes varies at least as much as that of their acyclic counterparts. As before, incipient radical stability and ground-state ring strain are the key factors, though cycloelimination sometimes comes into play. Let us first examine the effect of ground-state strain on the thermal lability of monocyclic azoalkanes. ATB, whose heat of formation is well established (Table VI) as –8.7 kcal mol⁻¹, is taken as the strain-free model

TABLE VI. Enthalpy of Formation of Azoalkanes (kcal mol^{-1})

compd	no.	ΔH_f (c or l)	ΔH_v	ΔH_f (g)	ref
	227	10.16 ± 0.53	8.70 ± 0.05	18.86 ± 0.53	123
	4	2.74 ± 0.83	9.53 ± 0.10 / 9.64[a]	12.27 ± 0.84	b
	AIP	–0.07 ± 0.84	8.58 ± 0.10 / 8.66[a]	8.51 ± 0.85	b
	AIP	10.9	8.5	19.5	122
	7	–9.59 ± 0.90	11.79 ± 0.05	2.19 ± 0.90	123
	ATB	–17.85 ± 0.86	9.34 ± 0.06	–8.51 ± 0.87	b
	ATB	–18.04 ± 0.65	9.34 ± 0.06	–8.70 ± 0.66	c
	ATB	–19.01	8.64[a]	–10.4	121
	10	54.7			121,d
	195	–41.3 ± 1.3	12.81 ± 0.05	–28.5 ± 1.3	b
	56	–62.9 ± 2.2	15.90 ± 0.15	–47.0 ± 2.2	b
	228	21.04 ± 0.64	14.88 ± 0.24	35.92 ± 0.69	c
	229	–5.34 ± 0.84	14.73 ± 0.05	9.39 ± 0.85	b
	230	–1.9 ± 1.1	11.96 ± 0.10	10.0 ± 1.1	b
	DBH	36.35 ± 0.62	13.21 ± 0.15 / 10.49[a]	49.56 ± 0.64	b
	231	4.9 ± 1.1	17.20 ± 0.13 / 16.70[a]	22.1 ± 1.1	b

[a] Determined by UV spectroscopy; see ref 121. [b] Engel, P. S.; Melaugh, R. A.; Mansson, M.; Timberlake, J. W.; Garner, A. W.; Rossini, F. D. *J. Chem. Thermodyn.* 1976, *8*, 607. [c] Montgomery, R. L.; Engel, P. S.; Leckonby, R. A.; Rossini, F. D.; Mansson, M.; Szilagyi, S.; Timberlake, J. W. *J. Chem. Eng. Data* 1979, *23*, 129. [d] McEwan, W. S.; Rigg, M. W. *J. Am. Chem. Soc.* 1951, *73*, 4725.

TABLE VII. Strain Energy of Azoalkanes Relative to a Strainless Trans Acyclic Model

compd	strain energy, kcal mol^{-1}	compd	strain energy, kcal mol^{-1}
AM(c)	5.74,[a] 6.5[g]	233	5.29,[a] 4.3[g]
AIP(c)	8[b,c]	230	6.26,[a] 8.4,[f] 7.8[g]
42c	12.6[d]	234c	11.39[a]
195	4.6[e]	234t	11.34[a]
56	10.7[e]	DBH	16.21,[a] 15.4,[b] 13.9[g]
228	27.7,[a] 24.5[f]	DBO	12.05,[a] 10.0[g]
232	4.46,[a] 2.3[g]	231	9.47,[a] 10.1,[b] 10.8[g]
229	3.57,[a] 2.9,[f] 2.7[g]		

[a] Force-field calculated value from ref 126a. [b] Reference 127. [c] Estimated. [d] Reference 98. [e] Reference 42. [f] Reference 128. [g] Force-field calculated value from ref 126b.

in computing the strain energy of three cyclic $\alpha,\alpha,\alpha',\alpha'$-tetramethylazoalkanes. Figure 10 shows the experimental strain energy of these compounds (cf. Table VII) added to their $\Delta H^{\ddagger}$ for thermolysis. The transition-state energy is essentially the same for ATB, **229**, and **230**, whereas **228** decomposes with considerably greater difficulty than its large ground-state strain would lead one to expect (see below). The discrepancy between ATB and **230**, which arises in part from the solvent effect on decomposition of *cis*-azoalkanes,[107] is considered too small to interpret. Thus activation parameters for **229** and **230** reveal
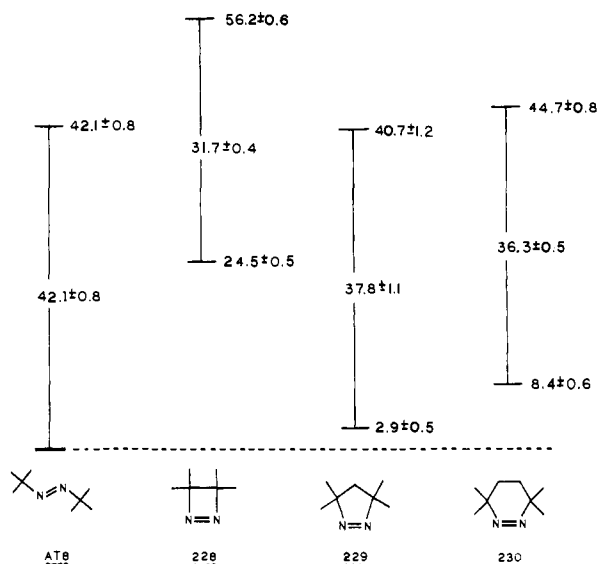
Figure 10. Experimental strain energy of cyclic azoalkanes added to their activation enthalpy for thermolysis. All values are in kcal mol⁻¹.

neither stabilization nor destabilization of their product biradicals.

1. Diazirines

As seen from the data in Table VIII, diazirines[149,150] exhibit activation energies for decomposition of about 30 kcal mol⁻¹ and A factors of approximately 10^{13}. Their low activation entropy and small substituent effect suggest a fundamentally different mode of decomposition from that of other azoalkanes. Despite considerable effort, little headway was made in understanding these compounds until Liu and co-workers[151-153] confirmed an old suggestion[149,154-157] that diazirines isomerize to diazoalkanes before losing N_2. Thus 3-butyl-3-phenyldiazirine (**254**) disappeared in Me_2SO at 100 °C three times faster than N_2 was evolved.[151] Intermediate **332** was detected spectroscopically,
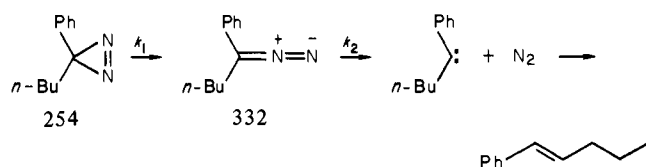
isolated, and shown to account quantitatively for the carbene produced.[153] Because acids catalyze decomposition of diazo compounds, thermolysis of **254** in acetic acid gave the same rate constant (k_1) for disappearance of **254** and formation of nitrogen. The contrast between the simple behavior of **332** and the more complex chemistry of **333** was attributed to steric hindrance.[153] Thus diazirine **251** leads to three kinds of products, depicted below. Whereas the thermolysis rate of **251** is not
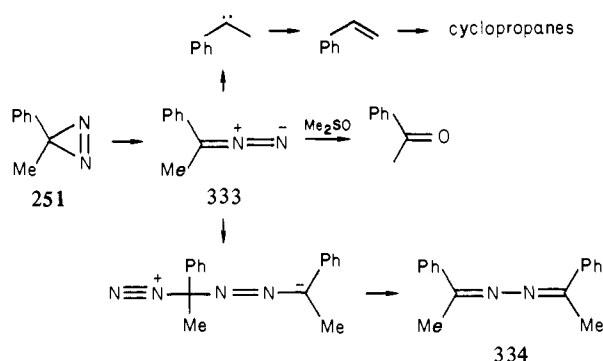
influenced by the nature of the solvent, the fate of **333** depends

on both solvent and concentration.[152] Formation of azine (**334**), a frequent reaction of diazo compounds, was shown[158] to proceed by a mechanism first suggested by Overberger[159] and illustrated above. 3-Halodiazirines rearrange only slightly faster than **251** or **254**, but the resulting diazo compounds decompose rapidly to carbenes. These carbenes can react not only with cyclohexene[160] but also with diazo compounds to give olefins.[158] It has recently been found that even carbenes such as chlorocyclopropylmethylene (**335**), which are expected to undergo rapid intramolecular rearrangement, can be trapped by olefins.[161]
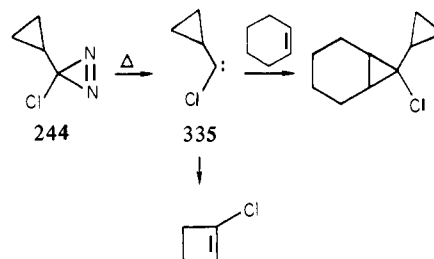
2. Diazetines

Despite their structural simplicity, diazetines are synthetically accessible by very few routes; consequently, their chemistry is only now coming to light. Even the early work on **255-257** (Table VIII) showed diazetines to be remarkably stable toward loss of nitrogen. That this stability arises from a high-lying transition state rather than a small degree of ring strain is apparent from Figure 10.

Among the reasons which can be advanced[128] for the high activation enthalpy of **228** and other diazetines, the possible role of orbital symmetry is particularly interesting. A significant barrier is anticipated for $[2_s + 2_s]$ cycloreversion,[162] but even the symmetry-allowed $[2_s + 2_a]$ mode may require considerable activation energy. It is now known[163] that loss of nitrogen from **336** and **337** is stereospecific and cis, so that certain mechanisms can be ruled out. Thus $[2_s + 2_a]$ cycloreversion may
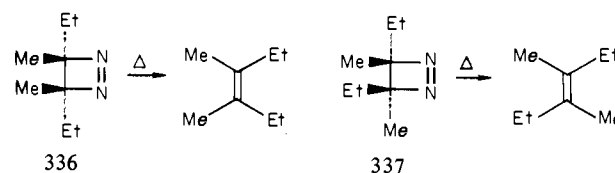
proceed by $2_a(N_2) + 2_s(olefin)$ but not by $2_a(olefin) + 2_s(N_2)$. Production of triplet excited olefin is possible energetically[128] and might even be anticipated from the results with dioxetanes;[164] however, this mechanism is not expected to be stereospecific.[163] Greene has pointed out that the stereospecificity of decomposition does not rule out a stepwise mechanism because diradical **338** could well undergo fragmentation prior to bond rotation.[183]

$r_{14} = 3.1$ Å, $r_{23} = 1.85$ Å
dihedral angles:

$\Theta_{1234} = 30°$
$\Theta_{5127} = 29°$
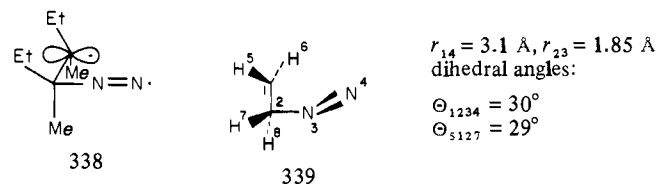
Indeed, a theoretical study[165] of diazetine fragmentation reveals that the preferred mechanism is unsymmetrical and involves diradicaloid **339**. This species lies at least 47 kcal mol⁻¹ below the transition state of the "allowed" $[2_s + 2_a]$ pathway, and it requires at most 7 kcal mol⁻¹ to lose nitrogen

Diazetine **340** was prepared recently,[166] and although it was stable at ambient temperature, pyrolysis could be effected at 125 °C. The exothermicity of decomposition was estimated from the known ΔH_f of **228** and is shown above. Concerted

TABLE VIII. Activation Parameters for Thermolysis of Monocyclic and Ring-Fused Azoalkanes[a]

compd	no.	$\Delta H^{\ddagger}$, kcal mol⁻¹	$\Delta S^{\ddagger}$, eu	E_a	log A	solvent	notes	ref
diazirines								
(R₁, R₂) = F, F	235			32.2 ± 0.7	13.1 ± 0.4	g	17 p	b
Me, Cl	236			27.2 ± 0.2	11.7 ± 0.1	g	9 p	c
				31.07	14.14	g		d
CCl₃, Cl	237			29.20	13.80	CCl₄, osc	8 p	e
Me, Me	238			33.2	13.9	g	8 p, 4 torr	f
				33.2	14.02	g	3 p	157
Et, Cl	239			30.45 ± 0.09	13.99 ± 0.05	g	8 p	g
				29.60 ± 0.04	13.81 ± 0.24	cyclohexene	8 p	h
Et, Br	240			28.09 ± 0.23	13.20 ± 0.14	anisole	8 p	h
n-C₃H₇, Cl	241			30.98 ± 0.06	13.98 ± 0.03	g	10 p	g
H₂C=CH, Me	242			25.6 ± 0.2	13.7 ± 0.1	CCl₄	8 p, rearranges	i
i-C₃H₇, Cl	243			30.59 ± 0.08	14.01 ± 0.04	g	9 p	g
c-(CH₂)₂CH, Cl	244			27.49 ± 0.11	13.64 ± 0.11	cyclohexene	6 p	160
Me₃C, Cl	245			29.50 ± 0.35	13.38 ± 0.20	g	9 p	g
Et, Et	246			31.89	13.73	g	5 p	j
c-(CH₂)₄	247			30.50	13.40	g	8 p	j
c-(CH₂)₅	248			30.5	13.4	g	9 p	j
Ph, Cl	249			28.00 ± 0.22	13.87 ± 0.13	cyclohexene	6 p	k
Ph, Br	250			27.36 ± 0.41	13.75 ± 0.40	cyclohexene	7 p	k
Ph, Me	251			28.50 ± 0.79	13.45 ± 0.46	Me₂SO	5 p	153
c-(CH₂)₆CH, Cl	252			29.11 ± 0.18	13.53 ± 0.11	cyclohexene	6 p	160
XC₆H₄, Cl	253			26.4-27.9	13.4-13.8	cyclohexene	various X studied	d, 160
Ph, n-C₄H₉	254			28.08 ± 0.09	13.26 ± 0.05	Me₂SO	11 p	153
diazetines								
tetrafluoro	255			38.95 ± 0.25	16.40 ± 0.13	g	5 p	l
tetramethyl	226	31.6 ± 0.4	0.3 ± 0.8	32.4 ± 0.4	14.33 ± 0.18	Ph₂O	8 p	128
	256	33.6	2.6	34.4	13.93	g	2 p	162
	257	33.2	5.6	34.0	14.59	g	2 p	162
pyrazolines								
	258	41.5 ± 0.5	11.3 ± 1.0	42.5 ± 0.5	15.92 ± 0.21	g	5 p, r	200
4-methylene	259	31.8 ± 0.1	−0.5 ± 0.2	32.8 ± 0.1	13.31 ± 0.05	g	5 p, r	222, 228
3-Me	260	40.1 ± 0.5	10.3 ± 1.0	41.1 ± 0.5	15.68 ± 0.22	g	5 p, r	200
4-Me	261	41.3 ± 0.2	11.0 ± 0.3	42.3 ± 0.2	15.84 ± 0.07	g	5 p, r	200
3-vinyl	262			32.2 ± 0.4	14.5 ± 0.1	g	4 p	197
4-spirocyclopropyl	392			39.9 ± 1.5		solution	nrd	232
4,4-dimethyl	263	42.3 ± 0.5	3.6 ± 0.9	43.3 ± 0.5	14.26 ± 0.20	g	5 p, r	200
3,3-dimethyl	264	39.1 ± 0.1	11.1 ± 0.2	40.1 ± 0.1	15.85 ± 0.05	g	5 p, r	200
cis-3,5-dimethyl	265	39.5 ± 0.4	9.7 ± 0.8	40.5 ± 0.4	15.54 ± 0.18	g	5 p, r	200
trans-3,5-dimethyl	266	39.3 ± 0.4	10.1 ± 0.8	40.3 ± 0.4	15.64 ± 0.17	g	5 p, r	200
4-isopropylidene	267	$k = 2.4 \times 10^{-4}$ s⁻¹ at 160.17 °C				g		228
3,3-dimethyl-4-methylene	268	$k = 2.1 \times 10^{-4}$ s⁻¹ at 160.17 °C				g		228
3,3,5-trimethyl	269	38.0 ± 0.7	9.1 ± 1.5	38.9 ± 0.7	15.41 ± 0.32	g	5 p, r	200
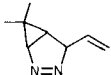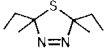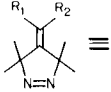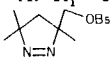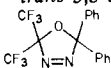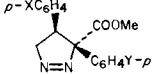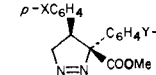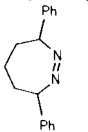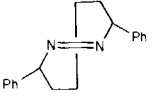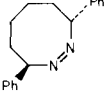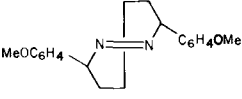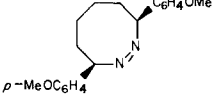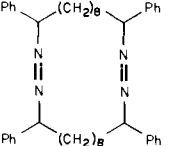
	No.							
	270	36.4 ± 0.2	14.2 ± 0.6	37.2 ± 0.3	16.47 ± 0.13	g	4 p, r	209
	271	37.5 ± 0.7	4.6 ± 1.5	38.5 ± 0.7	14.44 ± 0.34	g	3 p, r, ocs	209
	272	26.0 ± 1.0	3.3 ± 3.0			methylcyclohexane	ocs, nrd	238
pyrazolines								
cis-3,5-divinyl	273	22.3 ± 0.4	−4.5 ± 1.4	22.9 ± 0.5	12.28 ± 0.31	Ph$_2$O	4 p, r	196
trans-3,5-divinyl	274	25.2 ± 0.4	3.4 ± 1.3	25.8 ± 0.4	14.01 ± 0.29	Ph$_2$O	4 p, r	196
cis-3-ethyl-5-vinyl	275			31.3 ± 0.3	14.29	Ph$_2$O	3 p	196
3-isopropenyl-3-methyl	276			33.6 ± 0.4	14.7 ± 0.11	g	3 p	197
3-methyl-3-carbomethoxy	277	32.1 ± 0.2	6.2 ± 0.5			n-butyl phthalate	3 p, r	183
t-3,t-5-dimethyl-r-3-carbomethoxy	278	28.3 ± 0.8	0.5 ± 2.1			n-butyl phthalate	3 p, r	183
t-3,c-5-dimethyl-r-3-carbomethoxy	279	28.9 ± 0.5	2.4 ± 1.3			n-butyl phthalate	3 p, r	183
3,5,5-trimethyl-3-carbomethoxy	280	$k = 4.26 \times 10^{-4}$ s^{-1} at 109.4 °C				n-butyl phthalate		183
3-methyl-3-acetyl	281	30.6 ± 0.2	3.5 ± 0.5			n-butyl phthalate	3 p, r	183
t-3,t-5-dimethyl-r-3-acetyl	282	$k = 1.53 \times 10^{-3}$ s^{-1} at 109.4 °C				n-butyl phthalate		183
t-3,c-5-dimethyl-r-3-acetyl	283	28.3	2.4			n-butyl phthalate	2 p, r	183
3,5,5-trimethyl-3-acetyl	284	29.0	2.7			n-butyl phthalate	2 p, r	183
3-methyl-3-cyano	285	30.2	5.5			n-butyl phthalate	2 p, r	183
t-3,t-4-dimethyl-r-3-carbomethoxy	286	33.7 ± 0.2	7.8 ± 0.4			n-butyl phthalate	3 p, r	183
t-3,c-4-dimethyl-r-3-carbomethoxy	287	38.4 ± 2.0	14.7 ± 4.7			n-butyl phthalate	3 p, r	183
t-3-methyl-t-4-ethyl-r-3-carbomethoxy	288	38.0 ± 0.3	16.2 ± 0.8			n-butyl phthalate	3 p, r	183
t-3-methyl-c-4-ethyl-r-3-carbomethoxy	289	37.3	11.2			n-butyl phthalate	2 p, r	183
3-methyl-4-tert-butyl-3-carbomethoxy	290	35.7				n-butyl phthalate	nrd	183
3,3,5,5-tetramethyl	229	37.0 ± 0.6	4.9 ± 1.2	37.8 ± 0.6	14.49 ± 0.27	g	5 p, r	200
		39.1 ± 0.6	9.1 ± 1.4	40.1 ± 0.6	15.41 ± 0.30	Ph$_2$O	6 p, r	99
		37.7 ± 0.5	6.1 ± 1.0	38.5 ± 0.5	14.74 ± 0.23	PhEt	3 p, r	107
3,3,5,5-tetramethyl-4-keto	291	$k = 2.7 \times 10^{-5}$ s^{-1} at 205 °C						225
3,3,5,5-tetramethyl-4-methylene	292	39.7 ± 0.4	9.7 ± 0.9	40.7 ± 0.4	15.54 ± 0.19	g	3 p, r	224
		36.9 ± 1.0	4.1 ± 0.2			hexadecane	nrd	226
	293	24.8 ± 1.0	−1.0 ± 2.0			octane	nrd	217
	294	11.4	27.5			–	nrd	240
A: R$_1$ = R$_2$ = Cl	295	45.1 ± 1.1	14.3 ± 0.5			hexadecane	nrd	226
A: R$_1$ = H, R$_2$ = Me	296	40.3 ± 1.5	8.5 ± 0.3			hexadecane	nrd	226
A: R$_1$ = H, R$_2$ = Cl	297	32.8	−5.7	33.8	12.18	neat	2 p, r	340
	298	23.6	15.0	24.2	16.48	PhEt	2 p, r	107
A: R$_1$ = R$_2$ = Me	299	44.9 ± 1.0	12.6 ± 0.5			hexadecane	nrd	226
		38.7 ± 0.6	0.2 ± 1.1	39.7 ± 0.6	13.57 ± 0.25			225
A: R$_1$ = R$_2$ = CN	299a	39.0 ± 0.8	6.7 ± 0.2			hexadecane	nrd	226
A: R$_1$ = H, R$_2$ = COOEt	299b	41.4 ± 1.4	9.0 ± 0.3			hexadecane	nrd	226
A: R$_1$ = H, R$_2$ = t-Bu	299c	41.0 ± 1.2	9.7 ± 0.3			hexadecane	nrd	226
	300	31.8 ± 0.4	1.8 ± 1.0	32.8 ± 0.4	13.76 ± 0.22	HOAc	ionic	243

TABLE VIII (*Continued*)

compd	no.	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	E_a	log A	solvent	notes	ref
A: $R_1 = H$, $R_2 = Ph$	301	38.3 ± 1.0	7.6 ± 0.2			hexadecane	nrd	226
A: $R_1 = R_2 = COOEt$	302	38.0 ± 3.0	2.0 ± 0.7			hexadecane	nrd	226
pyrazolines								
trans-3,5-diphenyl	303	27.0 ± 0.6	3.4 ± 3.2	27.6 ± 0.6	14.03 ± 0.34	PhMe	8 p, r	23
trans-3,5-bis(*p*-chlorophenyl)	304	24.6 ± 0.4	−1.9 ± 1.3	25.4 ± 0.4	12.88 ± 0.28	PhMe	6 p, r	23
trans-3,5-di-*p*-tolyl	305	24.8 ± 0.3	−2.6 ± 1.0	25.4 ± 0.3	12.73 ± 0.22	PhMe	7 p, r	23
trans-3,5-di-*p*-anisyl	306	24.6 ± 1.2	−2.9 ± 3.4	25.2 ± 1.2	12.67 ± 0.72	PhMe	5 p, r	23
(structure)	307			24.0	14.8	C_6H_6	3 p, nrd, ocs	236
pyrazolines								
t-3,*t*-4-bis(carbomethoxy)-5,5-diphenyl-*r*-3-methyl	308	29.2		2.0		PhCN	4 p, nrd	247
(structure)								
X = Y = H	309	28.8	0.6		13.48	decalin	2 p	184
		29.9	2.3		13.85	PhNO$_2$	2 p	184
X = H, Y = NO$_2$	310	29.8	4.0		14.22	PhNO$_2$	2 p	184
X = NO$_2$, Y = H	311	30.6	3.4		14.10	PhNO$_2$	2 p	184
X = OMe, Y = H	312	29.8	2.2		13.83	PhNO$_2$	2 p	184
X = H, Y = OMe	313	30.8	4.9		14.42	PhNO$_2$	2 p	184
(structure)								
X = Y = H	314	30.3	3.6		14.14	decalin	2 p	184
		31.9	6.1		14.66	PhNO$_2$	2 p	184
X = H, Y = NO$_2$	315	30.2	4.5		14.33	PhNO$_2$	2 p	184
X = NO$_2$, Y = H	316	35.3	15.4		16.72	PhNO$_2$	2 p	184
X = OMe, Y = H	317	34.0	1.2		15.79	PhNO$_2$	2 p	184
A: $R_1 = R_2 = Ph$	318	39.5 ± 0.8	5.9 ± 0.2			hexadecane	nrd	226
six-membered azoalkanes								
(structure)								
3,3,6,6-tetramethyl	230	36.4 ± 0.1	12.0 ± 0.3	37.2 ± 0.1	16.00 ± 0.07	PhEt	3 p, r	107
		36.6 ± 0.3	11.8 ± 0.7	37.6 ± 0.3	15.96 ± 0.16	Ph$_2$O		99
		36.3 ± 0.2	12.0 ± 0.3			hexadecane		99
3,6-dicyano-3,6-dimethyl	319	21.3 ± 0.6	5.9 ± 2.2	21.9 ± 0.6	14.47 ± 0.50			27
		20.9 ± 0.7	4.1 ± 2.6	21.5 ± 0.7	14.08 ± 0.57	Et$_2$O	3 p, r	107
(structure)	320	15.3 ± 0.6	−3.9 ± 2.7	15.7 ± 0.6	11.43 ± 0.60	Et$_2$O	12 p	267
(structure)	321	$k = 4 \times 10^{-4}$ s^{-1} at −10 °C				Et$_2$O		*l*
(structure)	322	$k = 0.01$ s^{-1} at 200 °C				–	–	266
meso-3,6-diethyl-3,6-dimethyl	323	34.2 ± 0.4	6.9 ± 0.8	35.0 ± 0.4	14.87 ± 0.19	dodecane	6 p, r	*n*

cis-3,6-diphenyl	324	26.4 ± 2.0	1.0 ± 6.0	27.0 ± 2.0	13.5 ± 6.0	PhEt	3 p, r	142
		23.1 ± 1.2	4.4 ± 1.5			PhEt	error in data	107
trans-3,6-diphenyl	324a		0.4 ± 3.0	25.3 ± 1.1		PhEt	5 p	143
larger rings								
	325		8.17	29.7				270
	326	40.1 ± 0.4	11.9 ± 0.9	40.9 ± 0.4	16.02 ± 0.20	PhEt	3 p, r	107
	327	35.8 ± 0.4	8.2 ± 1.0	36.6 ± 0.4	15.17 ± 0.23	tetralin	3 p	271
	328	$k = 4.82 \times 10^{-5}$ s^{-1} at 60 °C		26.0		tetralin PhMe		112
	329			28.0		tetralin	3 p	271
	330			25.0		tetralin	3 p	271
	331	29.4	−1.1	30.2	13.11	xylene	2 p	*o*

[a] Note: See Tables I and II for abbreviations. [b] Neuvar, E. W.; Mitch, R. A. *J. Phys. Chem.* 1967, *71*, 1229. [c] Bridge, M. R.; Frey, H. M.; Liu, M. T. H. *J. Chem. Soc. A* 1969, 91. [d] Liu, M. T. H.; Toriyama, K. *Can. J. Chem.* 1972, *50*, 3009. [e] Liu, M. T. H.; Toriyama, K. *Int. J. Chem. Kinet.* 1972, *4*, 229. [f] Frey, H. M.; Stevens, I. D. R. *J. Chem. Soc.* 1962, 3865. [g] Frey, H. M.; Liu, M. T. H. *J. Chem. Soc. A* 1970, 1916. [h] Liu, M. T. H.; Chien, D. H. T. *Can. J. Chem.* 1974, *52*, 246. [i] Liu, M. T. H.; Toriyama, K. *Ibid.* 1973, *51*, 2393. [j] Frey, H. M.; Scaplehorn, A. W. *J. Chem. Soc. A* 1966, 968. [k] Liu, M. T. H.; Toriyama, K. *J. Phys. Chem.* 1972, *76*, 797. [l] Cosa, J. J.; Gsponer, H. E.; Staricco, E. H.; Vallana, C. A. *J. Chem. Soc., Faraday Trans. 1* 1973, 1817. [m] Berson, J. A.; Olin, S. S. *J. Am. Chem. Soc.* 1970, *92*, 1086. [n] Porter, N. A., Ph.D. Thesis, Harvard University, 1969. [o] Overberger, C. G.; Lapkin, M. *J. Am. Chem. Soc.* 1955, *77*, 4651.

$\Delta H_f = 64.4$ kcal mol^{-1} $\Delta H_f = 53.0$ kcal mol^{-1}

340
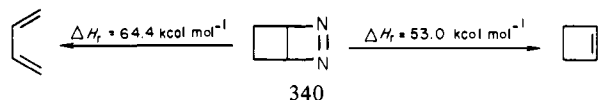
[$2_s + 2_s$] cycloreversion is forbidden just as in monocyclic diazetines, but fragmentation via a [$2_s + 2_s + 2_s$] pathway to give butadiene is symmetry allowed. Despite the orbital symmetry restriction on formation of cyclobutene and the greater exothermicity of butadiene formation, the product of thermolysis is in fact cyclobutene. The diradicaloid pathway should be more difficult for **340** than for **228** on account of the cyclobutane ring. Although kinetics for thermolysis of **340** have not been reported, the data available[166] suggest that it is actually somewhat less stable than **228**. Thus the pathway by which cyclobutene is formed remains a subject for future investigation.

Another interesting diazetine is compound **341**, which has only a transient existence at ambient temperature.[187] Despite the

341
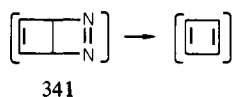
antiaromatic properties of cyclobutadiene, this product is formed far more rapidly from **341** than cyclobutene is from **340**. One can estimate ΔH_f of **341** as 121.6 kcal mol^{-1}, so its decomposition to cyclobutadiene[168] is considerably less exothermic (but is still 26.2 kcal mol^{-1}) than decomposition of **340**. The instability of **341**, even at -70 °C, is reminiscent of many failures to detect such azo compounds as **342** and **343**, which undergo rapid retrograde Diels–Alder reactions.[162,169] Apparently the [$2_s + 2_s + 2_s$] pathway is facilitated in **341** because of favorable alignment of the C–N bonds with the olefin p orbitals.

342   343

3. 1-Pyrazolines

Decomposition of pyrazolines is important from both synthetic and mechanistic viewpoints. Although thermolysis of these compounds can be used to prepare cyclopropanes (e.g., **344** → **345**),[170] photolysis is superior for this purpose.[171-177] The

344   345   346
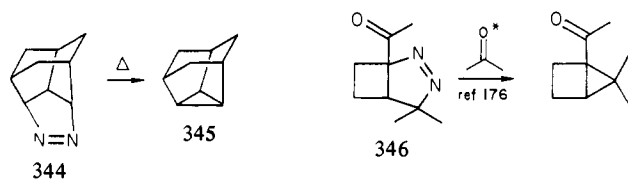
oldest and most convenient synthesis of pyrazolines is 1,3-dipolar cycloaddition of a diazo compound to an olefin. Because only activated olefins succeed in this reaction,[178] the first pyrazolines which were thermolyzed possessed electron-withdrawing groups on the α carbon. Compounds such as **347**, for example, produced cyclopropanes plus olefins arising from hydrogen or alkyl migration. From a synthetic viewpoint, it is important to note

347
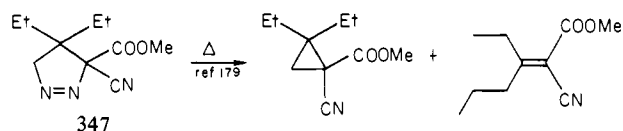
that some pyrazolines of this type (e.g., **348** and **349**) decompose below ambient temperature and lead only to olefins.[180-183] McGreer and co-workers suggested that olefin formation is a concerted process via transition state **350** and that conformational factors determine which isomer will form.[184-186] Although

348

349

350   351
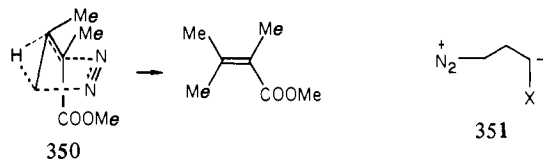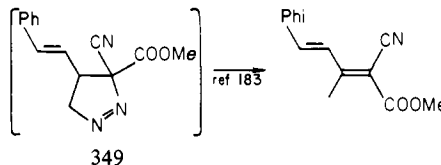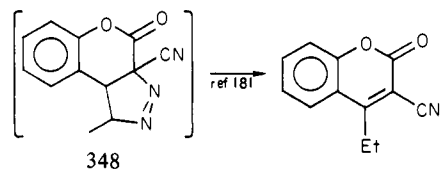
this mechanism is quite satisfactory,[180,187] the nature of the cyclopropane-forming reaction is controversial. A zwitterionic intermediate (**351**) has some attractive features, but it explains neither the widely divergent results for the stereochemistry[185] of this process nor the quantitative effects of solvent polarity[179] and substituents.[187] It was suggested recently that ionization of α-carbonylpyrazolines (**352**) leads to a tight ion pair or charge-transfer complex in which alkyl or hydrogen migration can occur.[186] The ion pair can proceed to ring system **353** which loses nitrogen by an electrocyclic process, as shown below. In

352   353
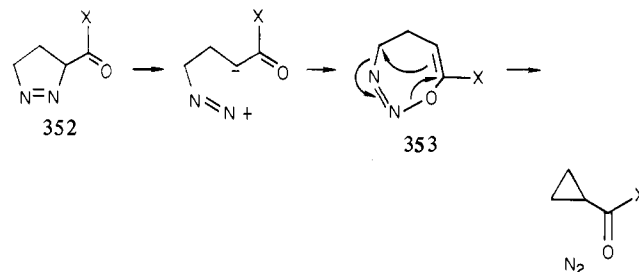
accord with experiment, this mechanism predicts that cyclopropanes will form readily from **354** but not from **355** or α-cyanopyrazolines.[188] Isomerization of **352** to **353** mildly resembles other recently reported 1,3 shifts of the azo group (cf. II.D); hence, spectroscopic detection of **353** may be possible.
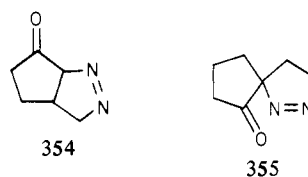
354   355

Since the decomposition of pyrazolines bearing α-electron-withdrawing groups is still not completely understood despite extensive investigation,[178-189] one might hope that simple pyrazolines would prove more tractable. It is generally agreed that the two classes are mechanistically different,[186,189,190] but, unfortunately, no completely satisfactory model for the decomposition of alkylpyrazolines has come to light[191] (see below). However, pyrazolines with α-phenyl or vinyl groups can be understood in terms of 1,3 diradicals, as we shall see in the following discussion.

Fifteen years ago, *trans*-3,5-diphenyl-1-pyrazoline (**303**) was reported to exhibit an activation energy for thermolysis of 11.6 kcal mol^{-1}.[192] Its melting point of 107–109 °C seemed inconsistent with such a low E_a, and indeed the value was later corrected[23] to 27.5 kcal mol^{-1}. The trans compound (**303**) was the only product isolated[192] from 1,3-dipolar cycloaddition of phenyldiazomethane and styrene, but this reaction was later

8% **357** + 92% **358**
44% **357** + 56% **358**
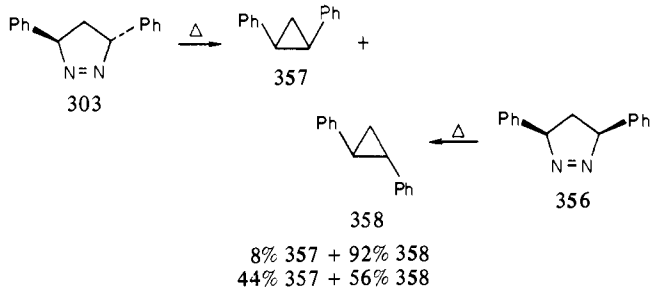
shown[193] to give a 60:40 mixture of **303** and **356**. Thermolysis of **303** was claimed[192] to produce exclusively **358**, but at least 6% **357** is actually formed[23,193] (the amount of **357** increases at higher temperature). Decomposition of the more labile cis isomer **356** produced **358** and **357** in a 56:44 ratio, exactly the figures obtained from *cis*-3,5-bis(*p*-anisyl)-1-pyrazoline.[23,194] In contrast to the earlier conclusion,[192] thermolysis of diphenyl-pyrazolines is clearly not a stereospecific reaction. The products can be rationalized by simultaneous cleavage of both C–N bonds to form the resonance-stabilized diradicals **359** and **360**. Ring
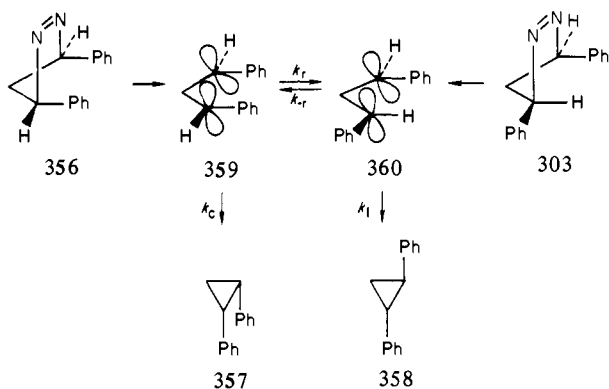
closure of **360** (k_t) is considerably faster than rotation (k_{-r}), giving **358** as the major product from **303**. On the other hand, rotation (k_r) of **359** with its interfering phenyl groups proceeds at a similar rate to ring closure (k_c) so that stereoselectivity is lost when **356** is the starting material.

Thermolysis of either *trans*- or *cis*-3,5-divinyl-1-pyrazoline (**273** and **274**) produces the same mixture of divinylcyclopropanes.

274 → 63% + 37%
273 → 62% + 38%
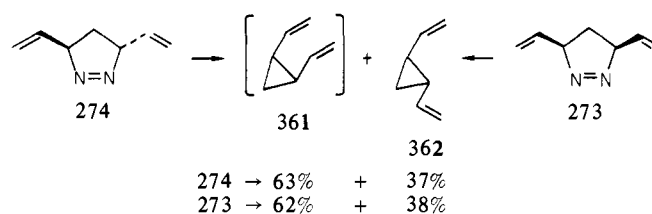
(The *cis*-cyclopropane **361** was analyzed as its Cope rearrangement product, cyclohepta-1,4-diene.)[195,196] In contrast to diphenylpyrazolines, the allylic diradicals equilibrate prior to ring closure. This result can be attributed to the smaller steric requirements of vinyl than phenyl and to the lower barrier to rotation of the vinyl group. Activation free energies for thermolysis of vinyl-substituted pyrazolines[196] are collected in Table IX. Substitution of vinyl for methyl decreases $\Delta G^{\ddagger}$ for thermolysis by amounts comparable to those in acyclic azoalkanes (Table III), implying that both systems proceed by the simultaneous but asynchronous decomposition mechanism. Crawford and Cameron[197] reached the same conclusion on the basis of isotope effects for the decomposition of **262**-d_2.

$\frac{k_H}{k_D} = 1.21$

262-d_2
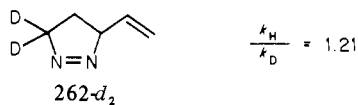
TABLE IX. Thermolysis of Selected
3,5-Disubstituted Pyrazolines

R^3	R^5	stereo-chem	$\Delta G^{\ddagger}$-(298 °C)^a	$\Delta\Delta G_1^{\ddagger b}$	$\Delta\Delta G_2^{\ddagger b}$
Me	Me	cis	36.6		
Me	vinyl	cis	29.3	7.3	5.7
vinyl	vinyl	cis	23.6		
Me	Me	trans	36.3		
Me	vinyl	trans	29.3	7.0	5.1
vinyl	vinyl	trans	24.2		

^{a} Calculated (kcal mol^{-1}) from data in ref 196. ^{b} Same definitions as in Table III; kcal mol^{-1}.

TABLE X. Thermolysis of Methylpyrazolines^a

pyrazoline	compd	$\Delta G^{\ddagger}$(240 °C), kcal mol^{-1}
unsubstituted	258	35.7
3-methyl	260	34.8
4-methyl	261	35.7
4,4-dimethyl	263	40.5
3,3-dimethyl	264	33.4
cis-3,5-dimethyl	265	34.5
trans-3,5-dimethyl	266	34.1
3,3,5-trimethyl	269	33.3
3,3,5,5-tetramethyl	229	34.5

^{a} Calculated from data in ref 197.

a. Alkylpyrazolines

Although pyrazolines which decompose to resonance-stabilized radicals are reasonably well understood, alkyl-substituted pyrazolines have proven more difficult with respect to both activation parameters and stereochemistry. As seen in Table X, α substitution of methyl groups has only a slight effect on thermal lability, whereas the results from acyclic azoalkanes would predict a decrease of 2.5 kcal mol^{-1} per added methyl group.[99] A possible explanation for this behavior is a decrease of the ground-state energy accompanying stabilization of the product diradical.[99] Whereas one force-field calculation[126a] (Table VII) concludes that tetramethylation of 1-pyrazoline reduces the ring strain by 0.9 kcal mol^{-1}, another calculation[126b] shows the effect to be in the opposite direction, in accord with an earlier suggestion.[178] If added methyl groups actually raise the ground-state energy, their influence on radical stability[59,198] must be minimal in order to rationalize the data in Table X. An unusually small α-methyl effect is also seen in bicyclic azoalkanes (cf. II.D). The high activation energy for 4,4-dimethyl-1-pyrazoline is thought to arise from steric hindrance to contraction of the "flap" angle of the ground-state "envelope" conformation as the C–N bonds break.[199]

An early result with particular significance in the pyrazoline field was Crawford and Mishra's report[199] that thermolysis of *cis*- and *trans*-3,5-dimethyl-1-pyrazolines (**265,266**) proceeded with predominant inversion at one reacting center. The diradical hypothesis which served nicely in the resonance-stabilized cases discussed above can explain only complete stereochemical scrambling or partial retention of configuration. Crawford rationalized this result on the basis of conrotatory closure of an intermediate π-cyclopropane (e.g., **363**). The following year
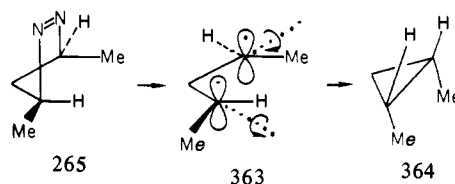
Roth and Martin[200] suggested that decomposition of 2,3-diaza-bicyclo[2.2.1]hept-2-ene (DBH) proceeded by single-bond cleavage, an idea which will also explain some of the pyrazoline

results.[201] A carbon-centered radical can in principle attack the diazenyl radical from the back, leading to single (364) or to double inversion of stereochemistry (365). In fact the latter process
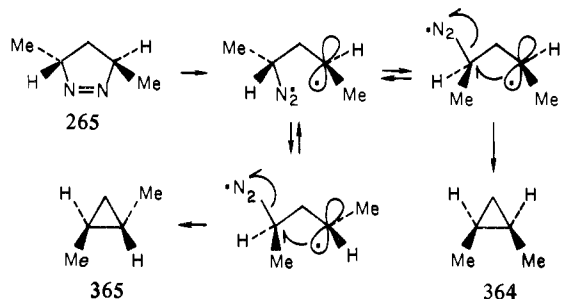

accounts for only part of the 365 which is formed, the remainder being due to double retention.[202] Another problem with this explanation is the considerable body of evidence[196,203] which shows that pyrazoline decomposition is not stepwise. On the other hand, a recent theoretical calculation[204,205] concludes that stepwise cleavage via a diazenyl radical is favored over synchronous loss of nitrogen.

A third possible rationalization of Crawford's results was invoked in bicyclic azo compounds, namely a recoil force caused by the departing nitrogen.[206] The resulting diradicals would be of inverted configuration at both centers and would ring-close faster than pyramidal inversion. Unfortunately, this hypothesis does not account for the fact that most of the product from 265 is 364, which arises from single inversion.

Of these three mechanisms, the one involving a π-cyclopropane (363) was considered in 1975[178] to be most consistent with the available data. The diverse stereochemical results were suggested to arise from conrotatory or disrotatory cyclization of antisymmetric and symmetric π-cyclopropanes whose energy order was a sensitive function of substituents. However, a more recent study[201] shows that all three of the mechanisms discussed thus far are inadequate.

In order to provide all possible stereochemical information on the decomposition of alkylpyrazolines, Bergman and co-workers[201] thermolyzed optically active 3-ethyl-5-methyl-1-pyrazoline, with the results shown below. The observation of considerable optical activity in the products (e.g., excess of 369 over 368) was taken as strong evidence against the intermediacy of π-cyclopropane, which possesses a plane of symmetry. Furthermore, neither the single-bond cleavage mechanism[200] nor the recoil force idea[206] can explain double retention from 366 (excess of 371 over 370).
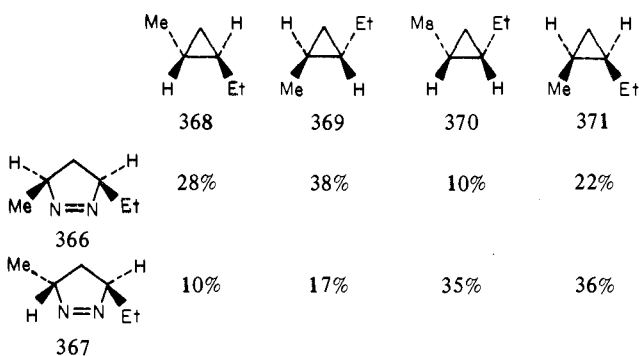
Having set forth reasonable arguments against all of the proposed mechanisms, Bergman[201] concluded that conventional diradical intermediates are unable to provide a satisfactory explanation of dialkylpyrazoline thermolysis.[207] Instead he suggested a reaction course consisting of a series of "snapshots" of the reacting molecule as it moves across a potential-energy surface. Nitrogen is extruded in a nonlinear fashion, causing clockwise pseudoconrotation of the ring bonds.

Planarization of the transient, which has pyramidal radical centers, takes place mainly by movement of the hydrogen atom. Least-motion considerations then serve to account for the relative amounts of products.

Although these ideas account for the results from 366 and 367, another explanation was set forth recently by Jean and Hiberty.[205] These authors proposed competitive stepwise reaction paths, one via a trans and the other via a gauche diradical. Disrotatory closure of the gauche diradical gave some double retention, and steric hindrance governed the relative importance of the two pathways. In perspective, the complexity of these "simple" pyrazoline thermolyses is noteworthy; however, one should bear in mind that most of the product is racemic and that the product composition reflects very small energy differences between competing pathways.

b. Ring-Fused Pyrazolines

Many ring-fused pyrazolines have been thermolyzed, and the results through 1972 have been nicely summarized by Mackenzie.[178] The goal in the larger ring compounds[208-212] was usually (e.g., in 372 and 373) to assess the importance of π-

cyclopropanes by restricting their formation; however, inversion of stereochemistry was still observed. This result is not inconsistent with any of the mechanisms discussed above.[210] Whereas 372 gave up to 19% of olefinic products, 373 produced exclusively cyclopropanes. Decreasing the size of the fused ring to three carbons led to a new reaction: cycloreversion to an olefinic diazo compound.[213,214] Although such intermediates had been isolated from pyrazolines containing electron-withdrawing groups,[215,216] it is only recently that the intermediacy of a simple olefinic diazo compound (374) was proven.[217]
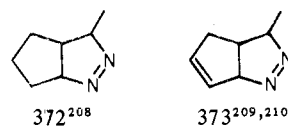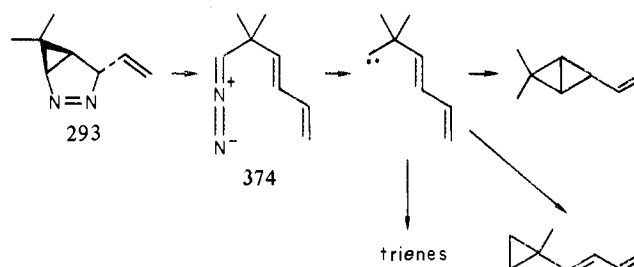

Decomposition of pyrazolines with a fused four-membered ring (375) occurs via both the carbene and diradical pathways.[218,219]
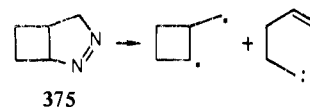

Thus the extent to which diazo compounds play a role in pyrazoline decomposition depends not only on substituents but also on fused ring size and on whether thermolysis or photolysis is employed.[172,179,199,213-219]

c. 4-Alkylidenepyrazolines

As mentioned at the outset, azoalkanes are useful precursors for diradicals of nearly any desired structure. The diradical trimethylenemethane (376)[220,221] is important both theoretically and as an intermediate in the methylenecyclopropane rearrangement; hence, generation of this species from 4-methylene-1-pyrazoline was investigated some years ago.[222,223] More recent work on a variety of 4-alkylidene-1-pyrazolines has produced a Pandora's box of results which are inconsistent with direct decomposition to free trimethylenemethanes. In the first

377   376   259
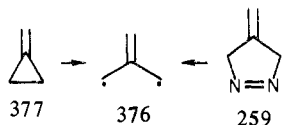
place, thermolysis kinetics of 4-alkylidene-1-pyrazolines (Table VIII) exhibits variations which do not readily correlate with structure.[224-226] The relative rate constants shown below, for example, suggest that resonance stabilization of **376** is responsible for the faster decomposition of **259** than **258**.

	258	259	229	292	298
k_{rel} (200 °C)	1.0	80	5.4	3.0	0.074
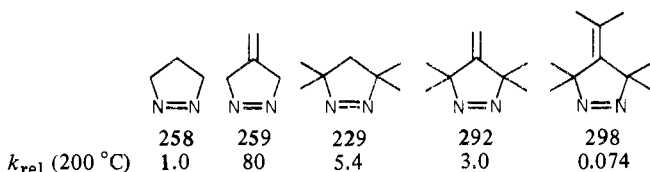
However, this factor of 80 is much less than one would expect from the substantial delocalization energy of trimethylenemethane (1.46 β). Thus the 4-methylene group should have nearly as great an effect as two α-vinyl groups (DE = 0.828 β each) which accelerate the rate by a factor of 10^6 (cf. Table IX). The most likely explanation is that the olefinic π bond and the breaking C–N bonds are nearly orthogonal, implying that the initial product is not trimethylenemethane but is a bis-orthogonal rotamer thereof.[226] This explanation is based on the failure of olefinic substituents (X) to accelerate thermolysis of **378**. Admittedly,

378
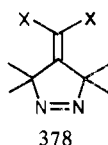
the tetramethylated pyrazolines may not be the best model for **259** on account of steric interference between cis methyl groups as the molecules bend into a sharply folded envelope conformation during decomposition. The only other rationalization which comes to mind is ground-state stabilization of **259**, an effect whose existence might be revealed by force-field calculations. In fact, ground-state energy differences become more appealing when trying to explain why **292** and **298** are actually slower than **229**.

259 is reported to decompose with $\Delta S^{\ddagger}$ = –0.5 eu.[222] Although this unusually low value has been attributed[222,227] to the spin-forbidden nature of decomposition directly to **376**, conclusions based solely on $\Delta S^{\ddagger}$ are hazardous. Pyrazoline **298**, for example, was said to exhibit $\Delta S^{\ddagger}$ = 0.2 eu,[225] but a kinetic study encompassing a fourfold greater temperature range gave $\Delta S^{\ddagger}$ = 12.6 eu.[226] It should also be noted that **259** is highly prone to tautomerize, a fact which can only complicate measurement of its decomposition rate.

Product studies in the alkylidenepyrazolines have proven to be at least as opaque as those of alkylpyrazolines. Crawford and co-workers reported[222,228] that α-labeled 4-methylene-1-pyrazoline (**259a**) gives methylenecyclopropane with a slight excess of label in the vinyl position, whether the label was deuterium or ^{13}C. Thus the results are not quite consistent with

	377a	377b	259a	379	259b
statistical	67%	33%			
* = ^{13}C	64%	36%			
* = D_2	60%	40%			
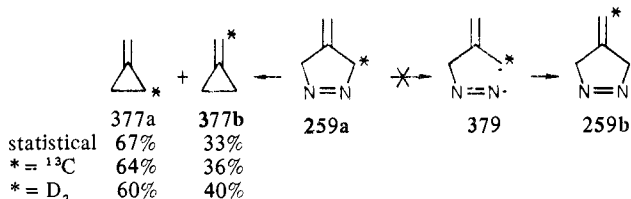
the intermediacy of free trimethylenemethane. α-Deuterium isotope effects and the fact that no rearrangement of label was detected in the starting material argue against a diazenyl in-

termediate (**379**).[228] (As we shall see in section II.D, intermediates of type **379** have been demonstrated in some cases.) Involvement of vibrationally hot species was rendered unlikely by the observation that the product composition was invariant on changing from gas to liquid phase and by the fact that **377a** turned up with too little label relative to the equilibrium mixture although it should have been the initial species produced. A similar experiment with **298a** led to the opposite result: more of the "least motion" product than expected on the basis of a planar trimethylenemethane.[229]

298a

	statistical	observed
	33%	67%
	67%	33%
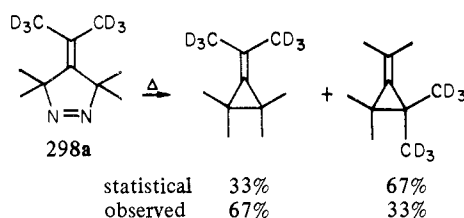
Thermolysis of **267** and **268** gave alkylidenecyclopropanes in the amounts shown below.[228] Although a common inter-

267   380   381, 37% from 267   19% from 268

268   382   383, 63% from 267   81% from 268
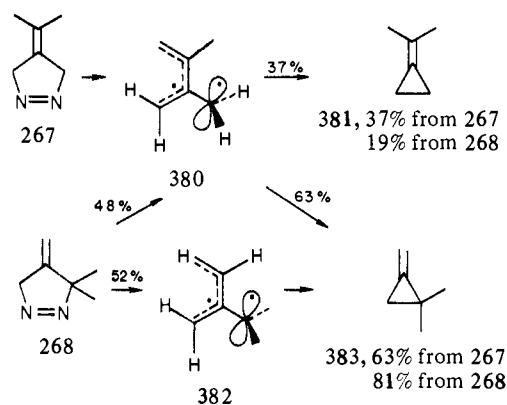
mediate was ruled out by the nonidentity of the product distributions, the so-called Chesick intermediates (**380**, **382**) could explain the results, provided that these species partition as shown above. Unfortunately, the same scheme did not correctly predict the product distribution of **259a**.[228]

A study[224] of **292**, though complicated by thermal interconversion of the alkylidenecyclopropanes, revealed that 52% of the initial product is **384**. If the "least motion" Chesick in-

292   384   385   386
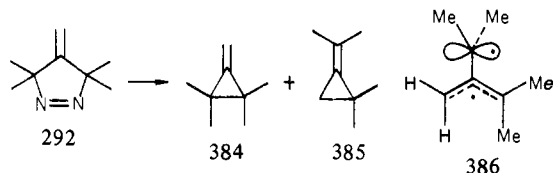
termediate **386** lies on the reaction pathway, the isopropylidene group in **386** must rotate out of the molecular plane 1.1 times faster than the methylene group, whereas in **380** the isopropylidene group rotates 1.70 times faster. This effect was rationalized on the basis of steric interactions.[224]

In an attempt to better define the nature of the intermediates involved, Crawford and co-workers examined thermolysis of a series of alkyl and deuterated 4-alkylidene-1-pyrazolines.[231] However no scheme analogous to that constructed for **267** and **268** could explain the product distribution from **387** and **388**.

387   389   390   388

387 → 80% + 20%
388 → 90% + 10%
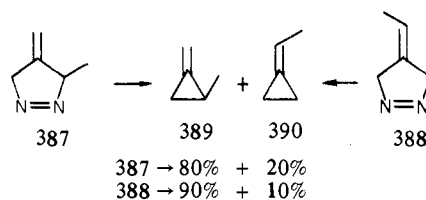
The deuterated species **388a** and **388b** gave the same ratio of **389**-d_2 to **390**-d_2 as did **388**, but the distribution of deuterium in **391a,b** depended on the precursor as shown below. Other

$$388a \rightarrow 75\% \quad + \quad 25\%$$
$$388b \rightarrow 20\% \quad + \quad 80\%$$
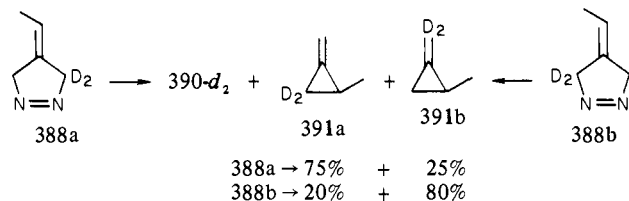
alkylidenepyrazolines exhibited the same tendency for the ring CH_2 anti to the substituent on the double bond to become the ring CH_2 of the alkylidenecyclopropane. It was concluded that the sequence in which the carbon–nitrogen bonds break plays an important role in determining the nature of the products. Although these reactions have turned out to be far more complex than anticipated, studies of chiral alkylidenepyrazolines which are now under way[231] may eventually allow an analysis of the type carried out on alkylpyrazolines.[201]

d. Spirocyclopropylpyrazolines

The timing of C–N bond breaking is an important consideration in thermolysis of the two isomeric pyrazolines **392** and **393**.[232]
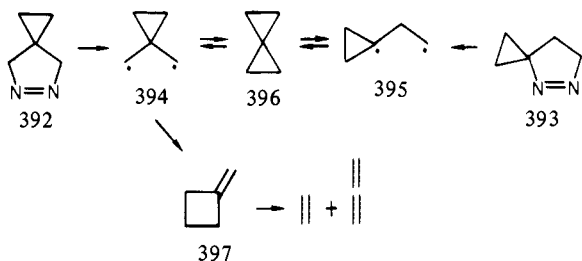
These compounds were selected as independent precursors to the diradicals **394** and **395** which arise in the pyrolysis of spiropentane (**396**). Gas-phase pyrolysis of **392** and **393** under a variety of conditions gave **396** as the major product plus lesser amounts of methylenecyclobutane (**397**) and its fragmentation products, allene and ethylene. When **392** was the precursor, the yield of **396** was independent of pressure, but the amount of fragmentation increased at lower pressures. On the other hand, the yield of both **396** and **397** was pressure dependent when **393** was the precursor. It was concluded that the unsymmetrical azoalkane **393** gives rise to vibrationally excited spiropentane but the symmetrical compound **392** does not. These observations were explained[232,233] in the following manner. **392** decomposes by simultaneous cleavage of both C–N bonds, passing through a symmetrical transition state in which coupling of the N–N vibration with vibrational modes of the organic fragment is very poor. Since the bond length in an azoalkane exceeds that in N_2, the nitrogen molecule is formed vibrationally excited, and it carries off much of the excess energy of decomposition. The unsymmetrical precursor **393** decomposes by stepwise C–N bond breaking, and the intermediate diazenyl radical may survive long enough to transfer most of the vibrational energy of the N=N moiety into the organic fragment. In this case nitrogen is extruded "cold" and the diradical **395** is vibrationally excited. Although this explanation requires that "hot" nitrogen be formed by thermolysis of symmetrical cyclic azoalkanes, no "hot" nitrogen has been detected to date, even from favorable cases such as tetramethyldiazetine.[234a]

e. Decomposition to Ionic Intermediates

Although azoalkane decomposition generally produces radicals, a number of recent papers invoke formation of ionic intermediates.[234b] For example, the variation in products from thermolysis of 1,3,4-oxadiazolines has been discussed in terms

of a dipolar ion.[235,236] As seen below, α-methyl groups tend to enhance formation of enol ether at the expense of epoxide; moreover, methanol suppresses the usual products and leads instead to ketals (e.g., **403**). A mechanism consistent with these results involves concerted loss of nitrogen to give carbonyl ylide (**404**), which can ring-close, undergo 1,4-proton shift, or be trapped by methanol (but not by other dipolarophiles).[236] Although no significant solvent effect was found, kinetic studies of ring-substituted analogues of **401** revealed $\rho^+ = -0.50$, indicative of slight positive charge development at the benzyl carbon.[236] The difference in products between compounds **399** and **400** is not strong evidence against this mechanism because resonance stabilization of **404** could suppress formation of enol ether from **400**.
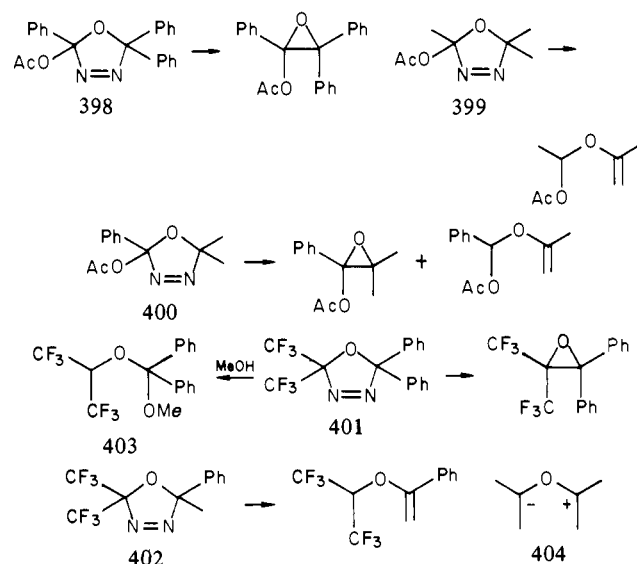

An interesting alternate explanation[235] for the difference between **399** and **400** is that 1,3,4-oxadiazolines decompose to diazenyl radicals (**405**) which undergo intramolecular hydrogen abstraction in competition with loss of nitrogen. Phenyl substitution would stabilize **405** and disfavor hydrogen abstraction.
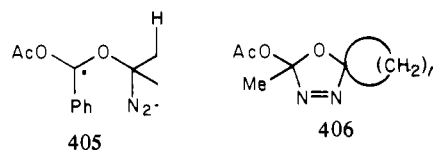

Although ring size effects in **406** are consistent with this idea, they are not inconsistent with direct formation of **404**. A problem with the alternate explanation is that the rate-enhancing effect of a phenyl group in **400** vs. **399** ($\Delta\Delta G^\ddagger = 4.1$ kcal mol^{-1}) is smaller than one might expect from studies of pyrazolines which decompose homolytically. Furthermore, the thermal instability of 1,3,4-oxadiazolines ($E_a \sim 24$ kcal mol^{-1}) is more reminiscent of pyrazolines with strongly electron-withdrawing groups than of alkylpyrazolines (see above). Since α-methoxy is not a very effective radical-stabilizing substituent,[23] this observation suggests decomposition directly to intermediate (**404**). Further insight into the mechanism by which these compounds decompose might be gained by examining **399** in methanol; if **405** really is the precursor to the enol ether, this product should continue to predominate.

1,3,4-Thiadiazolines have proven useful in synthesis of tetrasubstituted olefins,[237,238] as shown below.[239] Thermolysis of
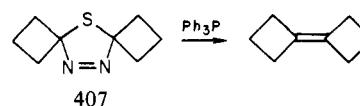

these compounds gives thiocarbonyl ylides which can ring close

stereospecifically[238,240,241] or be trapped by phenols, thiophenols, or 1,3-dipolarophiles.[242]

272
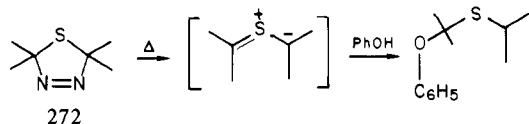
A number of azoalkanes which decompose via cationic intermediates have been reported by Allred and co-workers in recent years.[2,243-245] Pyrazoline 300 (Bs = p-bromobenzene-sulfonate), when solvolyzed in acetic acid, gave a quantitative yield of nitrogen plus the three products shown below.[243] The

300
408
409
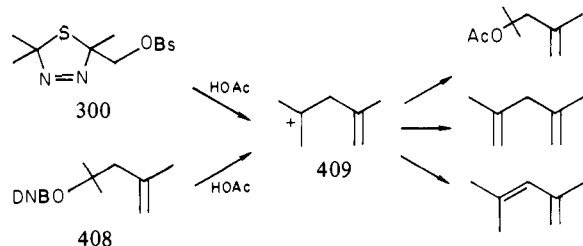
same mixture arose on solvolysis of 408 (DNB = 3,5-dinitro-benzoate), suggesting the intermediacy of carbenium ion 409 in both reactions. Neither 410 nor 411 was on the reaction pathway, as demonstrated by the absence of products expected from these species (e.g., 412 and 413). The 100-fold rate

410
411
412
413
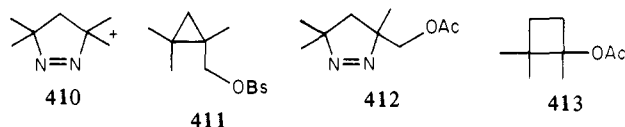
acceleration for solvolysis of 300 relative to neopentyl p-bromobenzenesulfonate is strong evidence for anchimeric assistance by the azo group, but little C(5)–N bond breaking occurs in the rate-determining transition state, even when an aryl group is incorporated at C(5) to stabilize the incipient carbenium ion.[244] All of the data are accommodated if transition state 414 and diazonium ion 415 lie on the reaction pathway. An earlier

300 →
414
415
→ 409
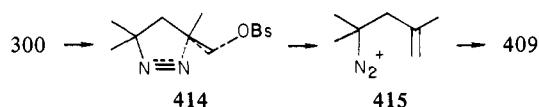
observation that BF₃ not only catalyzes decomposition of acetylpyrazolines but also increases the ratio of olefins to cyclopropanes is consistent with formation of an intermediate similar to 415.[248]

Although they are not pyrazolines, 416[245] and 417[2] should be mentioned at this point because they also undergo ionic decomposition. The flexible geometry of 417 allows participation

416
417
418
419
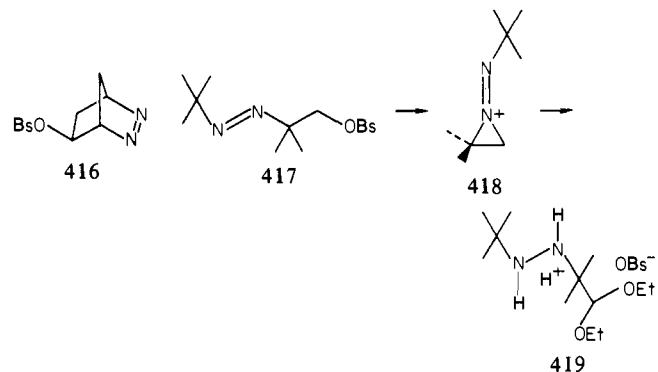
by the nearest nitrogen lone pair, giving rise to the cyclic tri-alkyldiazenium ion 418. In the absence of air, the ultimate product is the hydrazinium salt acetal 419 formed by proton shift

and addition of two molecules of ethanol. The effect of azoalkane geometry on solvolysis reactions is a worthwhile area of further research; three potentially interesting derivatives of DBH are shown below.

420
421
422
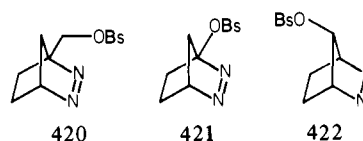
Anionic decomposition of pyrazolines is also possible, as shown by the conversion of 308 to allyl anion 424.[247] This

308
423
424
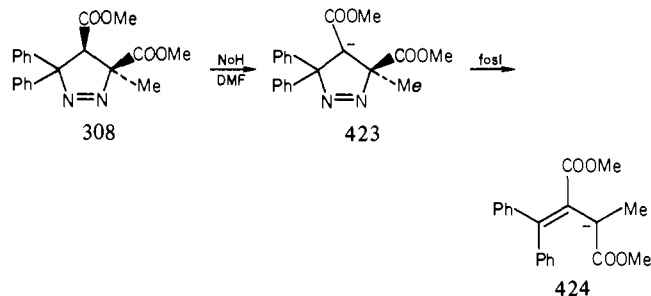
process is more facile than thermolysis of 308 by 12 kcal mol⁻¹, consistent with formulation of the anionic reaction as a retrograde $[4_s + 2_s]$ cycloaddition.

4. Six-Membered Azoalkanes

Although six-membered azoalkanes have not been studied as extensively as pyrazolines, a fascinating relationship between their structure and decomposition mechanism has come to light. In some cases (e.g., 342), loss of nitrogen proceeds by concerted cycloreversion, but in others (e.g., 425), production of a 1,4-diradical seems to dominate. Berson and co-workers[248]

342
425
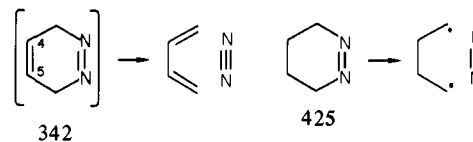
have proposed three criteria for concerted cycloreversion: an enhanced rate of nitrogen loss relative to a nonconcerted model, the absence of ring-closure products, and stereospecificity. Whereas azoalkanes of the type 342 meet all of these criteria,[249] the saturated analogues do not. Between the extreme cases represented by 342 and 425 lie azoalkanes with bent σ backbones and those which form "π,π-biradicaloid" hydrocarbons. These products are characterized by two approximately nonbonding π molecular orbitals containing a total of two electrons in the ground state.[250] Let us first discuss those azoalkanes which decompose to 1,4-diradicals.

It was noted over a decade ago that thermolysis of 323 occurs with high stereospecificity (>98% retention).[251] The

323
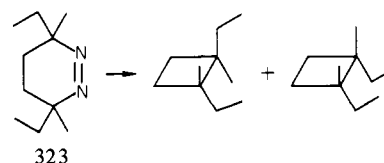
contrast between this result and the low stereospecificity of dimethylcyclobutane pyrolysis led Stephenson and Brauman[252] to postulate that vibrationally hot diradicals from azoalkanes undergo facile ring closure, whereas vibrationally equilibrated diradicals derived from cyclobutanes experience a barrier to closure and can therefore rotate. Beside the problem that thermolysis of 323 is endothermic by 16 kcal mol⁻¹, the diradical precursors used in this comparison were of a different sub-

stitution pattern. It is now known that azoalkanes **426** and **427** produce cyclobutanes with predominant loss of stereochemistry, along with a large amount of cleavage.[253] Since azoalkanes

$$426 \rightarrow 9.7\% + 16.3\%$$
$$427 \rightarrow 14.9\% + 8.9\%$$
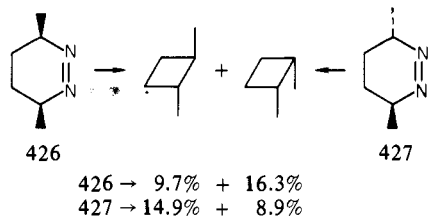
and cyclobutanes of the same substitution pattern give similar stereospecificities, the "hot diradical hypothesis" is no longer needed. The high stereospecificity in the case of **323** is readily understood on the basis of slower rotation rates for tertiary than for secondary radicals.[254-256]

Stereochemical studies have shown that thermolysis of azoalkanes **428** produces the same 1,4-diradicals as do the corresponding 1,1-diazenes **429**.[257] Although 1,1-diazenes have
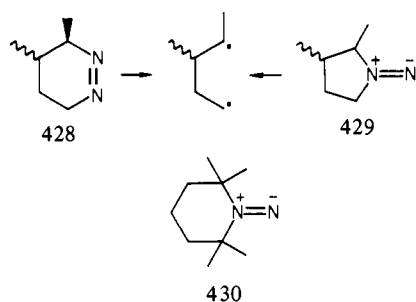
long been relegated to the status of "assumed intermediates," one of these species (**430**) has recently been observed spectroscopically.[258]

The stereochemistry of the thermolysis of **324** and **324a** resembles that of the analogous pyrazolines **303** and **356**[23,193] in that the trans isomer gives mostly trans ring closure while the cis isomer produces a mixture of cis- and trans-diphenylcycloalkanes.[142,143] Loss of nitrogen from **324** exhibits

$$324 \rightarrow 14.6\% + 30.1\%$$
$$324a \rightarrow 39.2\% + 1.7\%$$
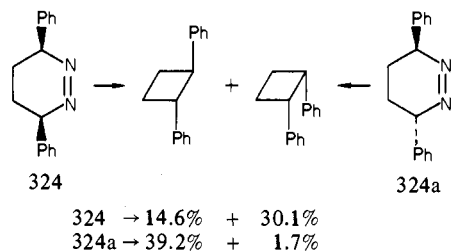
an activation volume of 5.5 cm³ mol⁻¹, indicative of simultaneous two-bond scission.[112] The resulting 1,4 diradical undergoes three competitive processes: ring closure, bond rotation, or cleavage to styrene. The much lower stereospecificity in the present ring closure relative to that in aliphatic analogue **323**[251] may result from benzylic stabilization of the diradicals, which decreases their recombination rate or increases their rotation rate.[143] Part of the explanation may also reside in the secondary vs. tertiary nature of the radicals.[254-256] Thermolysis of **319**, the cyclic analogue of azoisobutyronitrile (**10**), produces α-methylacrylonitrile plus trans-1,2-dicyano-1,2-dimethylcyclobutane, but the stereochemistry of the starting material is unknown.[259]

Radical delocalizing groups facilitate thermolysis of six-membered azoalkanes by approximately the same amount as in the acyclic series. Thus **319** exhibits $\Delta G^{\ddagger}(298\ °C) = 19.5$ kcal mol⁻¹, which is 13.4 kcal mol⁻¹ less than $\Delta G^{\ddagger}$ for **230**.[99,107] For comparison, the difference between azoisobutyronitrile (**10**) and ATB is 9.5 kcal mol⁻¹. A discrepancy of similar magnitude but in the opposite direction is found between **427** and **324a**.[143] $\Delta G^{\ddagger}$
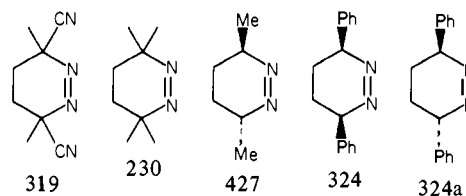

for **427** can be estimated as 33.3 kcal mol⁻¹ from data for **230** and analogous methylated pyrazolines (Table VIII). Whereas replacement of two methyls by phenyl in AIP leads to a $\Delta G^{\ddagger}$ decrease of 13.3 kcal mol⁻¹ (cf. third entry in Table III), the same change in **427** → **324a** lowers $\Delta G^{\ddagger}$ by 8.7 kcal mol⁻¹. Because of uncertainties in the experimental values, considerable variation in $\Delta S^{\ddagger}$ among the compounds, and our inadequate knowledge of ground-state energies, I am not inclined to speculate on the origin of these discrepancies. Trans azo compound **324a** decomposes 1.3 kcal mol⁻¹ more easily than the cis isomer **324**,[143] whereas the opposite result is obtained in the diphenylpyrazolines.[193] Since one set of results on **324**[107,261] differs considerably from all others on this compound,[112,142,260] they have not been used in making these comparisons.

Although **428** loses nitrogen even at 46 °C, both its thermal lability and the nature of the products are consistent with decomposition to a 2,2'-bis(allyl) diradical (**429**) which undergoes 2,2'-bond rotation faster than ring closure.[262] The relative yield
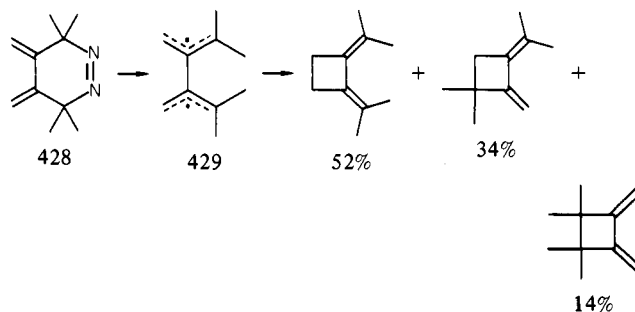

of these products is strikingly similar to that observed from azo-2-methyl-3-butene (**17**),[78] suggesting that steric hindrance to radical recombination governs the product distribution. The closely related azo compound **430** also decomposed to a bis-(allyl) diradical, though the only primary product in this case was **431**, presumably for steric reasons.[263] The parent bis(allyl)
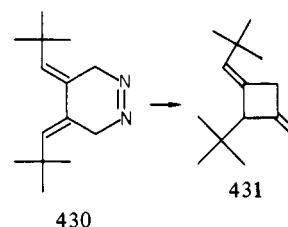
diradical "tetramethyleneethane" was observed by ESR during photolysis of 3,4-dimethylenecyclopentanone[264] and a cyclic analogue was generated by azoalkane photolysis[265] (cf. II.D).

Since a π bond between carbons 4 and 5 (**342**) changed the decomposition mechanism from diradical to concerted, Berson and co-workers[248] investigated azoalkanes with a bent 4,5 σ bond (**321** and **322**). High stereospecificity was observed for decomposition of the unstable azoalkane **321** to 2,5-heptadiene (**321a** → **432a**, **321b** → **432c**, **321c** → **432b**); hence it is a clear-cut case of concerted cycloreversion.[249] When the 4,5 bond was part of a cyclobutane ring, however, only two of Berson's criteria were met: stereospecificity (**322a** → **433a**, **322c** → **433c**) and absence of ring closure products.[286a] **322** was very much more stable than **321**; in fact, its $\Delta G^{\ddagger}$ for loss of nitrogen (32 kcal mol⁻¹) is the same as that of **230**. Nevertheless, the high stereospecificity argues convincingly for

321   432   322   433
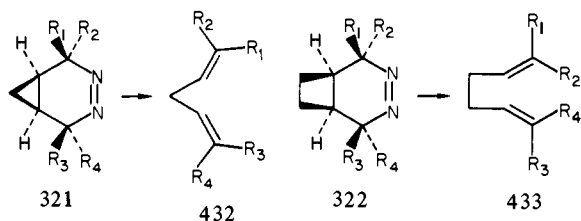
a, $R_1 = R_4 = $ Me; $R_2 = R_3 = $ H; b, $R_1 = R_3 = $ H;
$R_2 = R_4 = $ Me; c, $R_1 = R_3 = $ Me; $R_2 = R_4 = $ H

concerted decomposition of **322**.

If **322** undergoes concerted cycloreversion, it is reasonable to ask[248,253] whether some degree of concertedness survives even in the pure σ system (**425**). To investigate this question, Dervan et al.[253] studied the thermolysis of cis- and trans-**434**.


434t   \63%   434c   \65%
       diradical   diradical
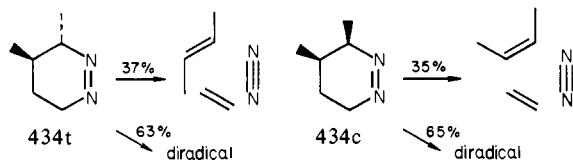
The cis stereoisomer was found to give a higher ratio of cis-2-butene to cis-1,2-dimethylcyclobutane than the trans isomer. Similarly, the trans-azoalkane gave a higher ratio of trans-2-butene to trans-1,2-dimethylcyclobutane than the cis-azoalkane. This observation of an extra component of stereospecific cleavage with retention suggests that some degree of concert does survive in thermolysis of pure σ cyclic azoalkanes. Whereas 36% of **434** decomposed concertedly, 45% of the parent compound (**425**) followed this pathway.[266b]

A thermally labile six-membered azoalkane (**320**) has been used to generate the π,π-diradicaloid hydrocarbon o-xylylene (**435**).[267] Although photolysis of **320** is more appropriate for

320   435   436
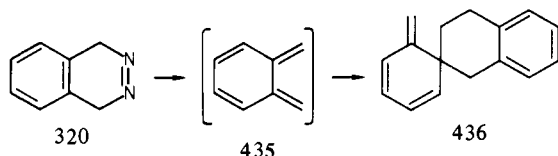
spectral observation of **435**, the isolation of dimer **436** from solutions of **320** warmed above –40 °C is good evidence for initial formation of **435**. **320** is more stable than 1,2-diazacyclohexa-1,4-diene (**342**) because cycloreversion in **320** destroys the aromaticity of the benzene ring; nevertheless, this reaction has the earmarks of concertedness. 2,3-Naphthoquinodimethane (**438**) is produced by warming a solution of **437**

437   438

439
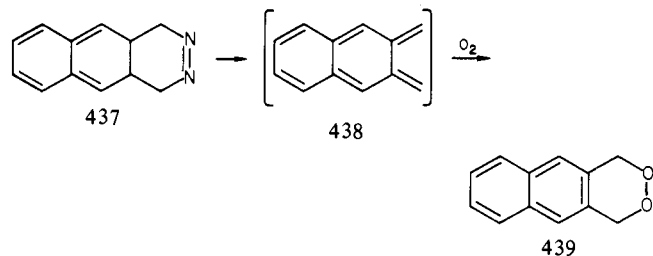
above –40 °C or by irradiating it in the cold.[268] Whereas **438** led to an intractable mixture of products in deaerated solution, it reacted cleanly with oxygen to give dioxin **439**. A cyclic o-xylylene has been prepared similarly[269] and will be discussed in section II.D.

Since the most recent work on thermolysis of cyclic azoalkanes larger than six members dates from several years ago,[270-272] the reader is referred to earlier reviews;[3,178] however, the photochemistry of these compounds will be covered in section IV.C. The preparation of macrocyclic azoalkane **440**

by the nickel-catalyzed cooligomerization of butadiene and acetone azine is appropriately mentioned here.[273]

440
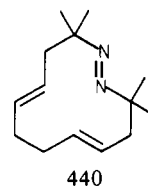
D. Bridged Bicyclic and Polycyclic Azoalkanes

Although DBH was prepared over 20 years ago,[274] the next lower homologue (**441**) has not yet been reported. The fact

DBH   441   442   443
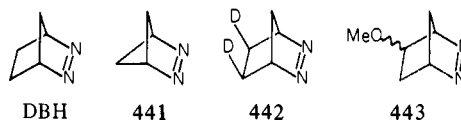
that thermolysis of DBH produces bicyclopentane[275] and not 1,4-pentadiene stands in noteworthy contrast to **434**, which decomposes in part by a concerted mechanism (see above).[253] The classic mechanistic studies on **442**[200] and **443**,[206] which showed predominant inversion of stereochemistry, have been reviewed elsewhere.[3,178,191] More recently, the DBH derivative **444** has been found by Corey and co-workers[276] to be a powerful mimic of prostaglandin endoperoxides.


444
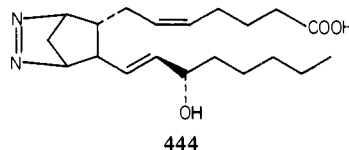
The synthesis of bicyclic azoalkanes is usually based on the Diels–Alder reaction of a cyclic diene with an azo ester.[13] Since hydrolysis of the adducts or their saturated analogues often requires strong base and high temperatures,[275] considerable interest has arisen in generating the azo group under milder conditions. In the earliest reports, this was achieved by metal reduction of trichloroacetates (e.g., **445**)[277,278] or by hydrogenolysis of benzyl esters.[281] Acidic hydrolysis of azophosphonoyl


445   446   447
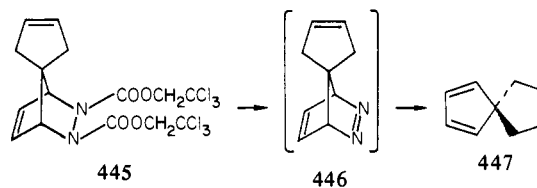
adducts bypasses the use of base, but a temperature of 100 °C is still required.[282] Masamune and co-workers[167] have recommended adducts of 1,2-bis(β-tosylethoxycarbonyl)diazene, which hydrolyze with alkoxide at 25 °C. More recently, it has been found that dialkylcarbamates can be cleaved under mild conditions with trimethylsilyl iodide[283] or the lithium salt of methyl mercaptan in HMPA.[284] The problem with these azo esters, even when irradiated to form the cis isomer,[285] is that they undergo the Diels–Alder reaction considerably slower than triazolinediones.[13,286] However, the adducts of the latter are again hydrolyzed only with strong base. A more easily cleaved adduct is obtained if sulfur replaces the 3-nitrogen in the triazolinedione, but unfortunately, this modification produces a less reactive dienophile.[287]

Berson and co-workers have carried out some very nice work over the last 8 years on the generation of cyclic trimethylenemethane **449** from bicyclic azo precursor **448**.[289,290] In the absence of trapping agents, triplet **449** undergoes dimerization,[291,292] but when **448** is decomposed thermally in a large

448   449
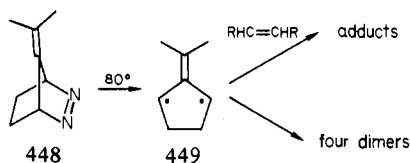
excess of conjugated olefin, dimer formation is suppressed and **449** is trapped efficiently.[293,294] Formation of adducts from **449** is favored by a larger barrier to intramolecular cyclization than in simple trimethylenemethanes. Decomposition of **448** was about 10^4 times faster[227] than DBH, in contrast to the smaller and variable rate changes found in the analogous alkylidene-pyrazolines (cf. II.C.3.c). The large rate enhancement is consistent with allylic stabilization of the proposed diazenyl diradical intermediate (**452**, see below). It is interesting to note that thermolysis of **450** is about 10^5 times faster than that of **448**.[295]

450   451
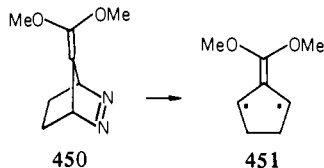
Since the HOMO of **449** is symmetric, concerted cycloreversion is orbital symmetry forbidden. The HOMO of **451**, on the other hand, is believed to be antisymmetric so that deazatization of **450** becomes thermally allowed. Substituent effects in thermolysis of alkylidenepyrazolines are small,[226] but only electron-withdrawing groups were employed and these are not expected to alter the ordering of MO's.

More detailed mechanistic studies on **448** reveal that it decomposes via a "cascade mechanism" in which singlet **449** forms initially and then intersystem crosses. When **448** was heated in a concentrated mixture of two olefins, analysis of the product composition allowed assignment to each "diylophile" of a relative gross reactivity.[296] The reactivity ratio for the pair acrylonitrile–dimethyl fumarate rose from a plateau of 0.06 at high olefin concentration to about 0.4 at 0.01 M olefin; moreover, addition of oxygen to the reaction mixture restored the high concentration limiting ratio. The authors postulated that **448** decomposes first to singlet **449**[297] which, if not trapped by added olefin, intersystem crosses to triplet **449**. In the absence of oxygen, the latter also reacts with olefins. This scheme is nicely supported by the regioselectivity of adduct formation as a function of concentration.[298] As shown below, singlet (S) and triplet (T) diyl can be trapped as fused (F) or bridged (B) adducts.

448   S   T
F   B
M = RHC=CHR
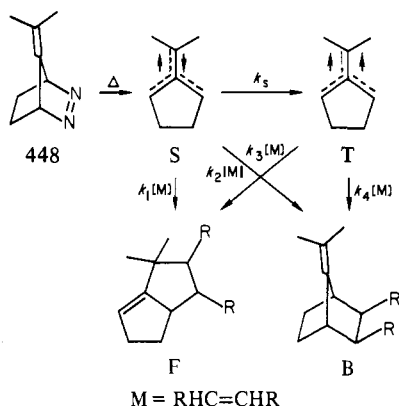
Kinetic analysis of the results showed that S is captured as a fused product with higher regiospecificity than is T; that is $k_2 \sim 0$ in some cases, but $k_3/k_4 = 0.66$. It was originally suggested[296,298] that S has a bisected geometry (**455**) which would produce a low bond order at the developing π bond in the transition state, leading to B but not to F. More recently,[290,295] the regiospecificity of cycloaddition was explained on the basis

of orbital symmetry control. This regiospecificity is of potential use in organic synthesis.[299]

In an attempt to generate a planar (**454**) and a bisected (**455**) trimethylenemethane from independent precursors, the trapping products from **448** were compared with those from isomer **453**.[300] If **454** were a discrete intermediate, it might give an


448   452   453

454   455
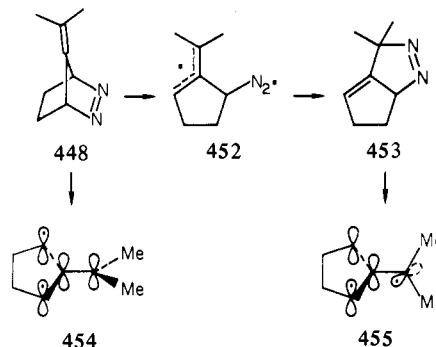
excess of bridged adducts (B) over fused adducts (F). The products were in fact identical, showing that any structural distinction between **454** and **455** was lost during the lifetime of the intermediate. A fascinating rearrangement of **448** to **453** was discovered during the course of this work. Since it occurred on thermolysis but not photochemically, a formal 1,3-sigmatropic shift was favored over recapture of the diradical by molecular nitrogen. The diazenyl radical **452** was postulated to lie on the reaction pathway, in accord with the orbital-symmetry-forbidden nature of concerted deazatization. Since 70% of **448** and virtually all of **453** decompose to **449**, the competing rearrangement has little effect on the product studies discussed above. Despite a careful search,[231] 1,3-rearrangement was not detected in **259, 268, 387**, and three other alkylidenepyrazolines or in 6-methylene-3,3,8,9-tetramethyl-1,2-diazaspiro[4.5]deca-1,8-diene.[300] It did occur, however, on heating **456**[301] or irradiating **457**.[302] Since these compounds are analogous to highly

456   457
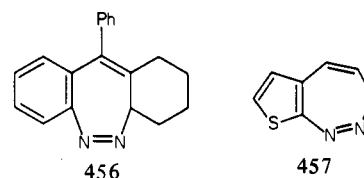
unsymmetrical arylazoalkanes[67] (cf. II.A.2), their rearrangement is less remarkable than **448** → **453**.

Beside trimethylenemethane **449**, other interesting diradicals have been produced from bicyclic azoalkanes. Thermolysis of **458**, for example, gave the bis(allyl) diradical **459**, which cyclized


458   459   460
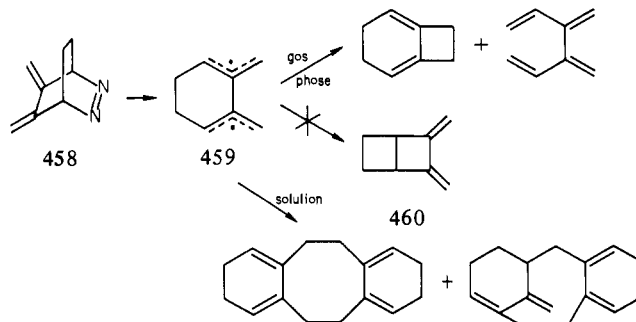
in the gas phase but dimerized in solution.[265] CIDNP evidence suggested that the dimers arose from two molecules of **459** in the triplet state, implying that intersystem crossing is far more probable in solution than in the gas phase. Azoalkane **461**-d_2 decomposed at 134 °C to an 87:13 mixture of **463** and **464**. From the random stereochemistry of deuterium in these products, it was concluded that diradical **462** was an intermediate

461-d_2 462   463

464

488   489
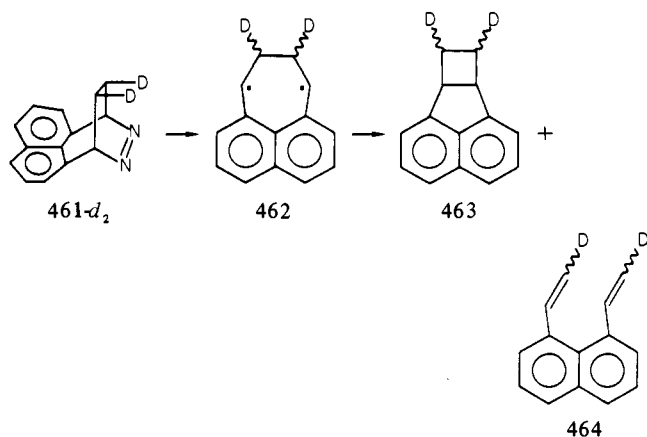
in the reaction.[303] Although 462 could not be trapped, its ESR spectrum was seen on irradiation of 461 at low temperatures.
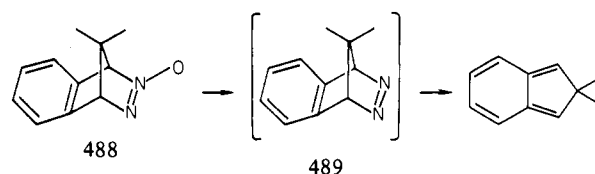
The thermal stability of bicyclic azoalkanes depends upon their structure in much the same way as in the monocyclic series. Thus the wide range of $\Delta H^{\ddagger}$ values (15–47 kcal mol^{-1}) seen in Table XI is largely due to orbital-symmetry considerations and to the effect of radical-stabilizing groups. As an example of the former effect, consider 468. Whereas thermolysis gave only

468   469
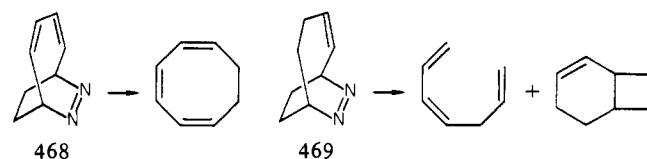
cyclooctatriene, as expected from a concerted pericyclic mechanism, unsymmetrical analogue 469 went in part to ring-closed product characteristic of a diradical mechanism.[111] The activation volume ($\Delta V^{\ddagger}$) for thermolysis of 468 (27.3 cm^3/mol) was similar to the 22.8 cm^3/mol of 475, which decomposes concertedly[304] (see below and Table XI). On the other hand, $\Delta V^{\ddagger}$ for 469 was only 2.2 cm^3/mol, consistent with a change in mechanism. Since these values of $\Delta V^{\ddagger}$ were calculated from solvent internal pressure, which roughly parallels solvent polarity (cf. I.A.4), they may not be the same as $\Delta V^{\ddagger}$'s obtained directly from the effect of external pressure on reaction rate. Thus monocyclic azoalkanes by the latter technique exhibit $\Delta V^{\ddagger} = 5$–7 cm^3/mol.[112] Whether this difference arises from a change in mechanism from concerted pericyclic deazatization in 468 and 475 to formation of diradicals in the monocyclic cases or whether it is an artifact of the different methods used will hopefully become clear when high-pressure studies on the bicyclic compounds[305] are completed. Replacement of one bridgehead proton in 468 with deuterium gave $k_H/k_D = 1.11 \pm 0.01$,[305] a result which agrees with other isotope studies on symmetrical azoalkanes[18,203,228] and thus supports two-bond cleavage. (A similar study of 445 would be of interest.) $\Delta G^{\ddagger}$ for the thermolysis of 468 (24.7 kcal mol^{-1}) was considerably larger than the $\Delta G^{\ddagger} < 14$ kcal mol^{-1} reported[162] for the orbital symmetry allowed case 343 (cf. II.C.2). Since decomposition of both compounds is exothermic by ~45 kcal mol^{-1}, the relatively high stability of 468 can be attributed to its forbidden (but nevertheless utilized) decomposition pathway.

Loss of nitrogen from 489 can be viewed as a retrograde [$4_s + 2_s$] or [$8_s + 2_s$] cycloaddition. Although this reaction is so facile as to preclude observation of the azoalkane, formation of 489 from an azoxy compound and the stability of 2,2-dimethylisoindene are noteworthy.[269]

Azoalkane 491 has been generated to investigate the interesting question of whether the existence of a suprafacial eight-electron component will retard deazatizatoin by an allowed six-electron pathway.[306] In fact, treatment of 490 or 492 with Si$_2$Cl$_6$ at 0 °C[305] led only to cyclooctatetraene and cyclo-

octadiene, respectively, the azo compounds never being observed. Since the rate-controlling step in this sequence is


490   491   492
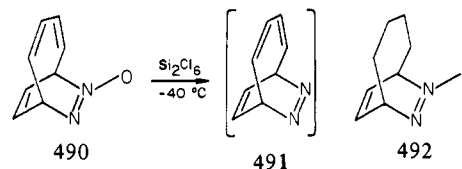
deoxygenation, it is not possible to determine the relative stability of 491 and the azoalkane derived from 492.[307a] One can say, however, that 491 is not highly stabilized by the butadiene bridge. Previous work[307b] on the 1,1-diazene analogous to 491 led to the conclusion that the existence of an eight-electron component did retard deazatization; however, the rate of competitive reactions could have influenced the efficiency of nitrogen loss. Although MO correlations[306] showed that deazatization was thermally allowed in both cases, this approach has also been questioned.[307a] If nitrogen extrusion rates from 491 and its dihydrogenated counterpart can be measured, it will be possible to settle the question of competing allowed and forbidden chelotropic reactions.

The effect of orbital symmetry is also apparent on comparing 493 and 494, both of which give octamethylsemibullvalene 495.[279] Whereas 493 decomposed immediately at –20 °C, 494 was about as stable as 3,5-divinyl-1-pyrazoline.[196] Deazatization

493   495   494
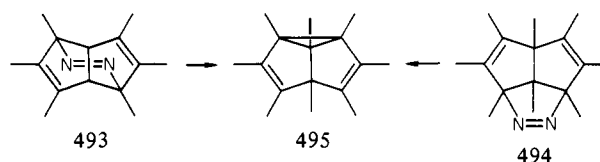
of 493 is a $_\pi 2_s + _\pi 2_s + _\pi 2_s$ concerted cycloreversion (one double bond is not involved), but pericyclic loss of nitrogen from 494 is an eight-electron forbidden process.

The 2 × 10^{11} deazatization rate enhancement caused by fusion of an exo cyclopropyl ring to a bicyclic azoalkane (470 vs. DBH) has been rationalized on the basis of symmetry-allowed synchronous nitrogen elimination and diene formation in the fused system.[308] Forcing the cyclopropyl ring closer to the bridging carbon by incorporation of a methylene bridge retards the decomposition rate so that 472 is only 9 times as fast as DBH.[309]

470   472   475
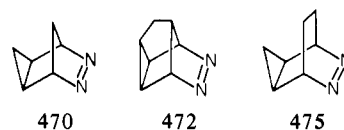
This effect is attributable to severe strain in the transition state for deazatization of 472 and to a less favorable alignment of its cyclopropyl orbitals with the breaking C–N bonds relative to those in 470. A photoelectron spectroscopic rationalization of these results has also been presented.[310] The negative $\Delta S^{\ddagger}$ for compounds such as 470 and 475 (–13 and –21 eu, respectively) was taken as indicating concerted decomposition;[311] however, more recent work[304] on 475 gave $\Delta S^{\ddagger} = +4.1$ eu. The original kinetics may have suffered from the presence of CuCl or from inaccuracies inherent in quantitative analysis by NMR. Despite this problem, it is still clear that 475 decomposes enormously faster than DBO.

Rastetter[280] took advantage of the mild conditions needed for deazatization of bicyclic azoalkanes with exo-fused three-

TABLE XI. Activation Parameters for Thermolysis of Bridged Bicyclic and Polycyclic Azoalkane
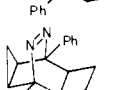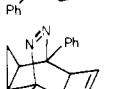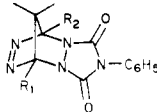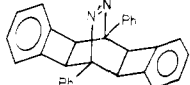
compd	no.	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	E_a	log A	solvent	notes	ref
	DBH	36.4 ± 0.2	6.5 ± 0.5	37.2 ± 0.2	14.81 ± 0.11		4 p, r	a
		36.0 ± 0.3	5.6 ± 0.6	36.8 ± 0.3	14.64 ± 0.13	g	5 p, r	200
5-exo-methoxy-DBH	443e	$k = 5.4 \times 10^{-4}$ s^{-1} at 160.0 °C				neat		206
5-endo-methoxy-DBH	443n	$k = 8.0 \times 10^{-5}$ s^{-1} at 160.0 °C				neat		206
7-isopropylidene-DBH	448		8.3 ± 0.7	28.8 ± 0.25	15.1	C_6H_6	nrd	227
	DBO	43.5 ± 0.03	8.4 ± 0.1	44.5 ± 0.03	15.29 ± 0.02		4 p, r	93
		45.0 ± 0.2	10.6 ± 0.4			hexadecane	5 p	128
5,6-dimethylene-DBO	458	$k = 1.0 \times 10^{-4}$ s^{-1} at 100.3 °C				C_6H_6		455
	460	27.4 ± 0.04	−7.9 ± 0.1	28.2 ± 0.04	11.64 ± 0.02	$Cl_2C{=}CCl_2$	3 p, r	c
1-methyl-DBO	465	43.9 ± 0.5	10.1 ± 1.0	44.9 ± 0.5	15.66 ± 0.22	hexadecane	5 p	128
1,4-dimethyl-DBO	231	43.7 ± 0.6	11.3 ± 1.2	44.7 ± 0.6	15.93 ± 0.25	hexadecane	5 p	128
1-vinyl-DBO	466	34.2 ± 0.8	7.7 ± 2.0	35.0 ± 0.8	15.05 ± 0.43	xylene	6 p	35
1,4-divinyl-DBO	467	28.8 ± 0.3	1.5 ± 0.8			xylene	7 p	35
	468	$k = 1.0 \times 10^{-4}$ s^{-1} at 48.4 °C				isooctane		111
	469	$k = 1.0 \times 10^{-4}$ s^{-1} at 90.4 °C				isooctane		111
	470		−13	17.7 ± 1.6		$CDCl_3$		308
	471	35.6	7.8			dodecane	nrd	327
	472		8.3	36.5 ± 0.3		g		309
	473		−5	23.3 ± 0.4		$CDCl_3$	5 p, nrd	309
	474		−6	19.6 ± 0.9		$CDCl_3$	5 p, nrd	309
	475	15.3	−18.7	15.9	9.10		2p, r	311
			4.1 ± 1.1	22.1 ± 0.4	14.1	isooctane	10 p, nrd, ose	302
	476	38.5	11.3	39.3	15.87		2 p, r	311
	477	41.9 ± 1.4	12.7 ± 3.2	42.5 ± 3.2	16.18 ± 0.69	?	3 p, r	314
	478	25.9 ± 0.4	13.2 ± 1.5	26.5 ± 0.4	16.12 ± 0.32	$CDCl_3$	4 p, r	280
	479	42.9 ± 4.4	21.8 ± 9.5	43.9 ± 4.4	18.18 ± 2.10	Ph_2O	6 p, r	319
	480	30.0 ± 0.3	−6.5 ± 0.6	30.8 ± 0.3	11.97 ± 0.13	Ph_2O	6 p, r	319
	481	$k = 5.8 \times 10^{-4}$ s^{-1} at 135 °C				$Cl_2C{=}CCl_2$		317
	482	$k < 1.3 \times 10^{-4}$ s^{-1} at 132 °C				$Cl_2C{=}CCl_2$		317

TABLE XI *(Continued)*

compd	no.	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	E_a	log A	solvent	notes	ref
	483	47.5 ± 4.0	15.4 ± 4.0	48.5 ± 4.0	15.81 ± 1.67	CD$_3$CN	error, r	b
R$_1$ = R$_2$ = Me	484	$k = 4.7 \times 10^{-4}$ s^{-1} at 99.5 °C				pyridine	d	320
R$_1$ = Ph, R$_2$ = Me	485	$k = 1.3 \times 10^{-3}$ s^{-1} at 84.5 °C				pyridine	d	320
R$_1$ = R$_2$ = Ph	486	$k = 9.8 \times 10^{-4}$ s^{-1} at 84.5 °C				pyridine	d	320
	487	35.8	5.0	36.7		Ph$_2$O	6 p	319

a Cohen, S. G.; Zand, R.; Steel, C. *J. Am. Chem. Soc.* 1961, *83*, 2895.   *b* Shen, K. *Ibid.* 1971, *93*, 3064.   *c* Pagni, R. M.; Watson, C. R. *Ibid.* 1974, *96*, 2291.   *d* Other temperatures were employed but the data were not sufficiently precise to calculate activation parameters.

membered rings to prepare *sym*-oxepin oxide **496**. Thermolysis of **478** proceeded with $\Delta H^{\ddagger}$ = 25.9 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 13.2 eu to give **496** in quantitative yield. Analogous syntheses of
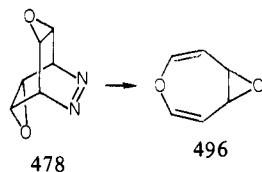
semibullvalene (**498**)[312] and dihydropyridines (**500**)[313] have also been carried out.
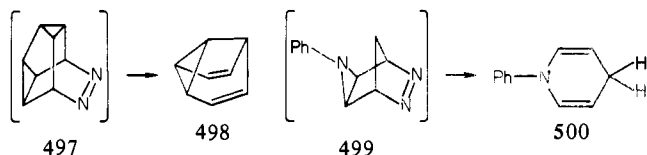
In contrast to the large effect of exo cyclopropanes, the endo isomers (e.g., **477**) exhibit no rate acceleration because the
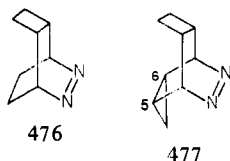
orbitals comprising the 5,6 bond are orthogonal to the breaking C–N bonds.[314] An exo-fused cyclobutane ring (**476**) accelerates thermolysis of bicyclic azoalkanes, but as in the monocyclic series (**322**) its effect is much less than that of a cyclopropane.[309,314,315]

Although several other azoalkanes related to DBH and DBO have been prepared, only crude kinetic data were reported in most cases. Despite this problem and the fact that the proper model compounds have not yet been studied, it is possible to make some statements about bridgehead substituent effects.
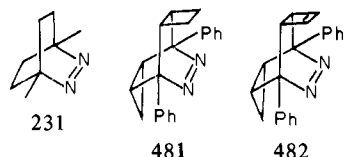

Thermolysis of **481** and **482** exhibited $\Delta G^{\ddagger}$(150 °C) = 31.3 and ∼32.6 kcal mol^{-1}, respectively, showing that these compounds are more labile than **231**[128] by 7.6 and 6.3 kcal mol^{-1}.[316] If one assumes that replacement of two methyls by phenyl should lower

$\Delta G^{\ddagger}$ by the same amount as in the acyclic series (11.7 kcal mol^{-1}), the endo-fused rings of **481** and **482** must exert a stabilizing effect. Similarly, **477** decomposes 2.2 kcal mol^{-1} less easily than **476**,[314] and **501** is nearly as stable as DBH, despite its two bridgehead phenyl groups. $\Delta G^{\ddagger}$(150 °C) for thermolysis of **479**, **480**, and **487** ranged from 32.6 to 33.8 kcal mol^{-1}, again
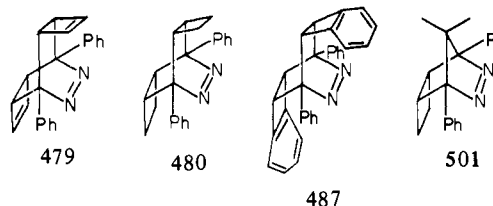
only 5.1–6.3 kcal mol^{-1} less than for **231**. Parenthetically, the small difference in stability among the latter three compounds demonstrates the absence of any pseudoaromatic interaction with the carbon–carbon double bonds.[318]

A contribution to the unexpected stability of the bridgehead phenyl compounds may come from geometric contraints which prevent full utilization of the benzyl resonance energy in the transition state for thermolysis.[317] One might assess the importance of this factor by rate studies of simple bicyclic azoalkanes **502** and **503**. If the special structure of **484–486**
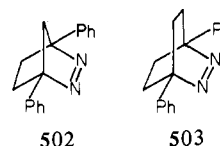
is overlooked, the crude kinetics available for these compounds[319] support the postulated steric inhibition of resonance.
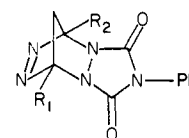
484, R$_1$ = R$_2$ = Me
485, R$_1$ = Me, R$_2$ = Ph
486, R$_1$ = R$_2$ = Ph

Introduction of the first phenyl group lowers $\Delta G^{\ddagger}$ by 2 kcal mol^{-1} while the second has only one-tenth of this effect. However, $\Delta G^{\ddagger}$ for **484** is 5.7 kcal mol^{-1} lower than DBH, suggesting that considerable diradical stabilization is already present.

A recently prepared set of azoalkanes which relate to this discussion is DBO and its bridgehead vinyl analogues **466** and **467**.[35] The reported $\Delta G^{\ddagger}$(150 °C) for these compounds (40.5,

466

467
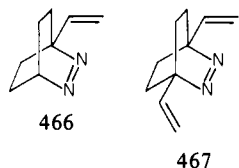
30.9, and 28.2 kcal mol^{-1}, respectively) leads, by the definitions in Table III, to $\Delta\Delta G_1^* = 9.6$ kcal mol^{-1} and $\Delta\Delta G_2^* = 2.7$ kcal mol^{-1}. Comparison of these figures with the 13.7 and 4.8 kcal mol^{-1} found in the series AIP, 184, and 17 reveals a smaller effect of α-vinyl groups in the bicyclic compounds. Thus steric inhibition of resonance may operate here too, though its magnitude appears to be less than that found in the bridgehead phenyl series. It was concluded[35] that 466 decomposes by asynchronous stretching of the C–N bonds but that the symmetrical compounds DBO and 467 probably follow the simultaneous, synchronous mechanism for loss of N$_2$. Since incorporation of one vinyl group seems to change the decomposition mechanism, it is better in principle to use a less powerful radical-stabilizing substituent. A recent study employing bridgehead methyl groups gave relative rate constants at 240 °C for DBO, 464, and 231 of 1.0, 2.13, and 5.06 (cf. Table XI). Although the effect of methyl groups was surprisingly small, these results are more consistent with synchronous decomposition to a diradical than with stepwise homolysis.

Thermolysis of bicyclic azoalkanes containing a fused cyclopropane ring gives exclusively products of ring opening, in support of the concerted mechanism.[308,320] On the other hand, cyclobutane rings tend to survive in the products, as shown by the examples below. There are some cases, however, in which

477

481

501
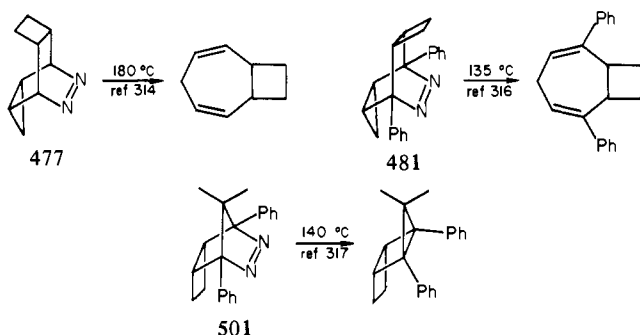
the primary products are unstable at the reaction temperature,[316-319] as illustrated for DBO[93,321,322] and 479.[318a,318b]

DBO

479

Thermal instability of the products has made investigation of 476 particularly difficult. This azoalkane was at first[311,323] thought to give only cis,cis-1,5-cyclooctadiene (504) on thermolysis; however, later work[324] revealed the presence of anti-tricyclooctane (505). It was concluded[324] that 476 decomposes to
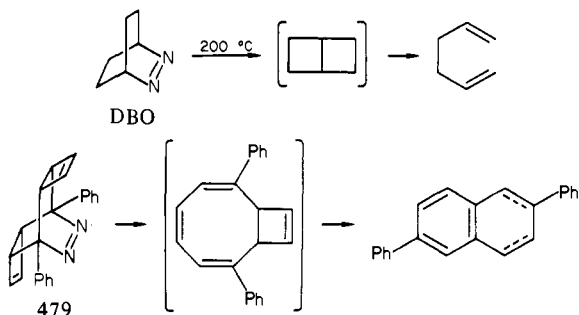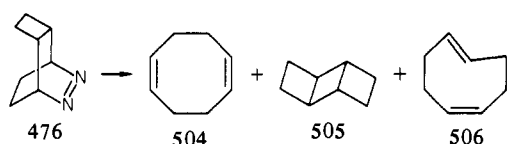

476   504   505   506

a diradical, in accord with Berson's criteria[248] (cf. II.C.4). A recent reinvestigation[325] of this compound was prompted by the fact that 506 is a major product from thermolysis of 505. Since the latter reaction proceeds via a diradicaloid, the near absence of 506 from pyrolysis of 476 indicates noninvolvement of the same diradicaloid. The dominant reaction of 476, as in its bicyclic analogue 322,[66] is a concerted [$\sigma_s + \sigma_s + \sigma_s$] cycloreversion to 504.[325]

Another compound for which the primary product is thermally labile is azoalkane 471. Whereas an early study[326] reported

471   507
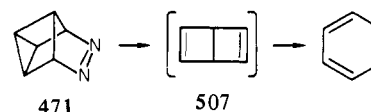
its transformation to benzene on thermolysis at 160 °C, more recent work[327] has shown that heating 471 in the presence of 9,10-dibromoanthracene (DBA) produces chemiluminescence. The emission was identified as fluorescence of DBA excited by energy transfer from triplet benzene. Since Dewar benzene (507) yields triplet benzene on thermolysis, 507 is implicated as the intermediate in the conversion of 471 to benzene.

Bicyclo[2.2.2]azoalkanes seem to be particularly resistant to thermal decomposition; for example, DBO has a half-life of 3 h at 230 °C. As seen in Table VIII, DBO possesses a ring-strain energy of about 11 kcal mol^{-1} so that its transition-state energy (strain + ΔH^*) is 55 kcal mol^{-1}. Comparison with Figure 10 reveals that all of the ground-state strain must be present at the transition state, presumably because the bond angles remain constricted until late on the reaction coordinate.[99] It has been noted[128] that a pair of α-methyl groups lower ΔG^* for thermolysis of DBO by only 1.7 kcal mol^{-1}, whereas their effect in the acyclic series is 5 kcal mol^{-1}. This effect can be rationalized, in accord with one set of force-field calculations,[126a] if the ground state of DBO is stabilized by added methyl groups. However, another set of calculations[126b] shows the opposite trend, suggesting that α-methyl groups fall short in their ability to stabilize the transition state.[99] An experimental determination of ΔH_f of DBO should resolve this discrepancy.

More complex azoalkanes which contain the bicyclo[2.2.2] skeleton have proven similarly resistant to thermolysis. Thus diazabasketene (508), which was intended as a precursor to cubane,[328] led to intractable materials under most pyrolysis conditions. Flash-vacuum pyrolysis at 500 °C, however, pro-

508   509
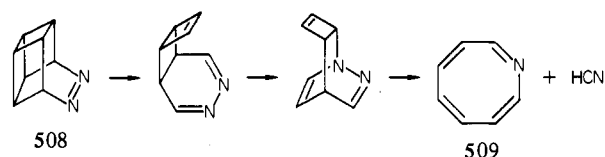
duced the unstable heterocycle azocine (509) probably via the intermediates shown above.[329] 510 yielded no volatile products on heating at 175 °C, though it disappeared with a half-life of 50 min. Flash-vacuum pyrolysis at 430 °C produced 511 and

510   511   512   513
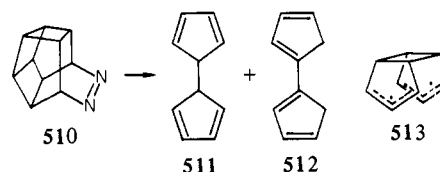
512 in 60% yield via diradical 513.[330] Heating 514 at 320 °C for 3.5 h or subliming it through a quartz tube at 535 °C led only to starting material.[331] Similarly, efforts to eliminate nitrogen from 515 proved unsuccessful.[332] Thus these last two compounds lie at the upper end of a long stability scale whose lower limit is polycyclic azoalkanes which are not even observable (e.g., 446, 491, 493).
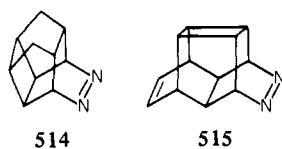
514   515

III. Spectroscopy

Since absorption spectra of azoalkanes have been covered in detail,[86,333] the present brief discussion will be confined to the more recent advances in this area. Most azoalkanes exhibit a weak n,π^* band in the 300–400-nm region with the extinction coefficient for cis isomers being about ten times higher than that for trans isomers. Tables of λ_{max}[7,334] as well as UV spectra[5,66,128,333,335-337] of various azoalkanes have been published. As shown by comparing AIP(c) with ATB(c) and 229 with 230, λ_{max} of the cis compounds shifts toward longer wavelength as the C—N=N angles expand (see also Table V). Particularly

AIP(c)	ATB(c)	229	230
λ_{max}, nm 382	447	327	380
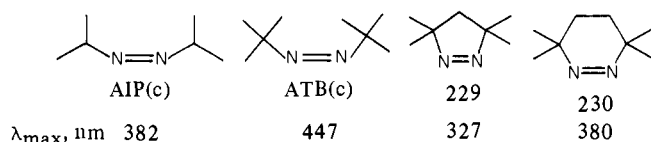
striking is the steady progression found in the series of cis-1-azobicyclo[2.m.n]alkanes, which exhibit the following λ_{max} (nm): [2.1.1], 404; [2.2.1], 423; [2.2.2], 444. These values suggest that the λ_{max} of such compounds may serve to indicate steric size of various R groups. Baird et al.[338] have rationalized this trend on the basis of greater repulsion between n orbitals and hence higher energy of the HOMO with increasing C—N=N angles. Whereas the correlation of λ_{max} with bond angle seems to hold for the azoalkanes shown above, it breaks down for three- and four-membered rings (λ_{max} 366 and 347 nm, respectively).[128,336] Extension of the calculations below the lower limit of 105 °C used in the early work[338] reveals that the singlet excitation energy passes through a maximum around $\angle$C—N=N 100° and that diazirine behaves exceptionally because its HOMO is qualitatively different from that of the larger ring compounds.[339]

Fluorescence from pyrazolines[340,341] and bicyclic azoalkanes[342,343] has been known for a number of years, although the difference in spectral shape between DBO[343] and its dimethyl analogue 231[336] remains unexplained. A more recent study of 19 azo compounds revealed fluorescence quantum yields (Φ_f) ranging from $<10^{-4}$ to 0.7 and lifetimes (τ_f) up to 740 ns.[336] Values of both Φ_f and τ_f are often much lower in hexane, methanol, and water than they are in acetonitrile because of hydrogen abstraction and hydrogen bonding. Thus a large isotope effect is seen for fluorescence quenching of 231 by CH$_3$OH vs. CH$_3$OD (Φ_D/Φ_H = 10).[344] Since DBO forms a perfectly stable protiodiazenium cation,[345] the reported fluorescence quenching of 299 by H$_2$SO$_4$[336] can be attributed to protonation of ground-state azoalkane as well as to an excited-state interaction.

Whereas the absorption maxima of azoalkanes undergo a blue shift with increasing solvent polarity, the emission maxima show an even more pronounced red shift with concomitant smearing out of the vibrational fine structure.[336] The 0–0 bands, on the other hand, are not especially sensitive to solvent polarity. As in aromatic azo compounds,[346] transfer from nonpolar to polar solvent is exothermic for both ground and excited states. Ground-state dipole moments ranging from 3.2 to 3.9 D have been measured for cis-azoalkanes,[84,305,347] but the effect of electronic excitation is uncertain. However, solvent effect studies on pyridazine and 9,10-diazaphenanthrene suggest a smaller dipole moment in the n,π^* excited state than in the ground state.[348]

Due to the complete absence of phosphorescence from azoalkanes, their triplet states have, until recently, been exam-

ined only by indirect means.[7] A triplet state (probably n,π^*) of DBH has been located at 60 kcal mol^{-1} from the effect of sensitizer triplet energy on the decomposition quantum yield.[349,350] A similar study was carried out on a 4-alkylidene-1-pyrazoline,[340] but this technique is inapplicable to most acyclic azoalkanes because their triplet state fails to decompose (see below). Two groups have deduced a triplet energy (E_T) of about 53 kcal mol^{-1} for the acyclic compounds from the variation of energy-transfer rate constants with a series of sensitizers.[335,351] More recently, the differential electron scattering spectrum and trapped electron spectrum of azomethane both revealed a band at 63 kcal mol^{-1} with an onset of 53 kcal mol^{-1}.[352] This value of E_T is in accord with the 53–55 kcal mol^{-1} obtained from the oxygen-induced direct absorption from S_0 to T_1.[353] A very weak $S_0 \rightarrow T_1$ absorption was also seen in 256, 471, and 472, and irradiation into these bands produced the characteristic triplet photochemistry of these compounds.[354] The lack of phosphorescence from any simple azoalkane, even when the triplet state is populated by energy transfer,[355] indicates rapid radiationless decay of T_1. Although this process is thought to occur by rotation of the T_1 state followed by intersystem crossing to the ground state,[114-116,120] the reason for its high rate in some rigid azoalkanes remains obscure.

A number of reports have appeared on the photoelectron spectroscopy of azoalkanes, and a table summarizing many of the results has been published.[336] The lowest ionization potential (IP) ranges from 8.06 to 9.75 eV, depending on the C—N=N bond angle and on the substituents present. An attempted correlation of IP with UV λ_{max} shows considerable scatter[334] unless the compounds being compared are very closely related.[356]

The infrared spectra of simple azo compounds including cis- and trans-azomethanes have been examined in detail.[83,357-360] Although hexafluoroazomethane was assigned the cis structure on the basis of an electron diffraction study,[361] more recent IR and Raman data lend strong support to the trans structure.[362] Microwave spectroscopy on cis-azomethane[84] and DBH[347] provides the molecular structure of these compounds. Other structural determinations of azoalkanes are available from X-ray analysis[363-365] and NMR spectroscopy.[366,367]

IV. Photochemical Reactions

Excellent reviews on photochemistry of azoalkanes are available, covering the literature through 1972.[3,5,178,368] A discussion of azoalkane triplet states[7] and another on thermal and photochemical cycloelimination of nitrogen[8] are of more recent vintage. The focus here will be on the mechanistic aspects of azoalkane photochemistry and on the most recent progress in this field.

A. Acyclic Azoalkanes

1. Direct Irradiation

a. Cis–Trans Isomerization

Irradiation of trans-azomethane at 25 °C in benzene produces the cis isomer with a quantum yield ($\Phi_{t\rightarrow c}$) of 0.42; the reverse reaction proceeds with a $\Phi_{c\rightarrow t}$ of 0.45.[369] Similar results were obtained for cis-azoisopropane, for which $\Phi_{t\rightarrow c}$ = 0.50 and $\Phi_{c\rightarrow t}$ = 0.54 in water.[90] The fact that photoisomerization of azomethane occurs even at -196 °C[82] and the observation that $\Phi_{t\rightarrow c}$ and $\Phi_{c\rightarrow t}$ for azoethane are both about 0.3 in a frozen matrix independent of wavelength[370] imply that the excited state involved cannot possess a significant barrier. As in the thermal reaction (see II.A.5), a number of theorists have considered the mechanism of azoalkane photoisomerization. Rotation is clearly the preferred pathway for the $^3(n,\pi^*)$ state and the most likely for the $^1(n,\pi^*)$ state.[114-116,120] The situation for higher electronic

SCHEME I

$$A \xrightarrow{h\nu} A^*$$

$$A^* \xrightarrow{k_r} N_2$$

$$A^* + M \xrightarrow{k_d} A + M$$

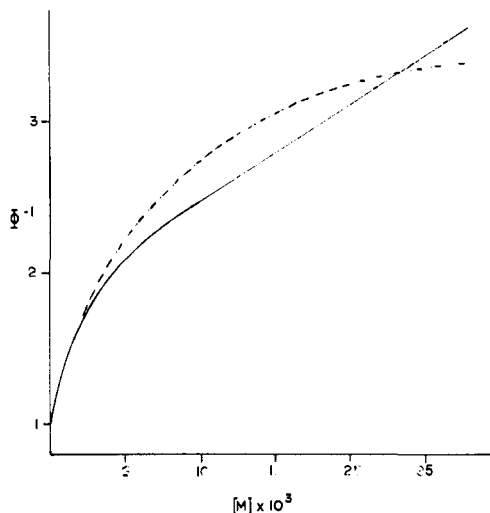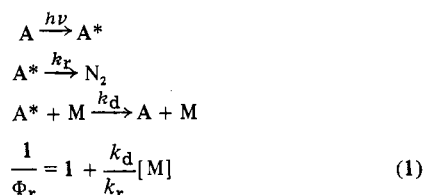$$\frac{1}{\Phi_r} = 1 + \frac{k_d}{k_r}[M] \qquad (1)$$

Figure 11. Stern-Volmer plot for photochemical decomposition of *trans*-hexafluoroazomethane[375] (—) 27 °C, 366 nm, and azoiso-propane[90] (- -) 25 °C, 334 nm. The data of ref 90 were converted to gas concentration and corrected for the lower quenching efficiency of CO_2 (0.34) than AIP (1.0).

states is uncertain, though fewer calculations have extended into this region.

Not only is direct photoisomerization of the lower azoalkanes an efficient reaction, but the cis isomers are moderately stable substances which can be isolated and studied independently. Tertiary azoalkanes, on the other hand, yield thermally labile cis isomers[27,95] whose decomposition to nitrogen has been discussed above. It is important to realize that most of the nitrogen and free radicals produced by irradiation of tertiary azoalkanes in solution does not come from direct photolysis; instead, trans → cis isomerization is the principal light-induced reaction.

b. Mechanism of Direct Photolysis

The photolysis of azoalkanes in the gas phase has been known for 40 years as an efficient means of producing free radicals.[371,372] Concerted decomposition to nitrogen plus alkane is of negligible importance.[368,372] Early workers rationalized the observed decrease in quantum yield for nitrogen formation (Φ_r) at higher pressure in terms of Scheme I.[372] According to this "excited molecule mechanism" an unspecified excited state of the azoalkane (A*) either dissociates (k_r) or is deactivated (k_d) by an inert gas molecule M. The Stern-Volmer equation (eq 1), which is derived from this scheme, predicts that a plot of $1/\Phi_r$ vs. [M] should be linear with slope k_d/k_r. Drewer[368] has nicely summarized the older data, which show a higher value of k_d/k_r with increasing complexity of the azoalkane. Since most of the early plots were indeed linear, the only remaining question seemed to be the identity of A*.

The plausible idea that A* is the vibrationally equilibrated $^1(n,\pi^*)$ state (A_0^1) was rejected for the particular case of azoisobutane.[335] (The superscript indicates electronic state and the subscript vibrational state.) Here the dissociating species was quenched by inert gas so easily that its lifetime had to be at least 700 ns; however, the failure of azoisobutane to fluoresce meant that A_0^1 survived for less than 1 ns.

SCHEME II
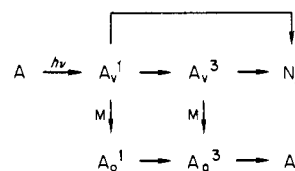
SCHEME III
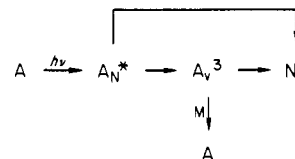
Further study of Φ_r as a function of pressure revealed Stern-Volmer plots which were not linear; in fact, previously observed deviations[373,374] of the intercept from unity are now recognized[375] as curvature in the low-pressure region. Pritchard and co-workers[375,376] confirmed the curvature reported for hexafluoroazomethane[377] and AIP[90] (cf. Figure 11). The shape of these Stern-Volmer plots immediately suggests dissociation from a species of long lifetime (Lo) and one of short lifetime (Sh). Although insufficient data were presented to discern curvature in the plot for azoisobutane,[335] the dissociating species with a 700-ns lifetime is safely assumed to be Lo. It is therefore this species for which the assignment as A_0^1 was rejected. For hexafluoroazomethane and AIP, the initial slope in Figure 11 (3.6 × 10^3 M^{-1}) again suggests that Lo ($\tau > 11$ ns) is not A_0^1, but the slope at high pressure is small enough (<65 M^{-1}) that Sh might be A_0^1.

Perhaps the most obvious scheme[378] which comes to mind on viewing Figure 11 is that Sh is the lowest excited singlet state reached by light absorption and that Lo is the derived triplet state. This mechanism (Scheme II) was first suggested by Wu and Rice[377] and later supported by Pritchard et al.[375] The two dissociating species (A_v^1 and A_v^3) were postulated to be vibrationally excited in order to explain deactivation by inert molecules and to be consistent with the observed temperature and wavelength effects (see below). No fluorescence or phosphorescence is observed because A_0^1 intersystem crosses rapidly to A_0^3 which decays radiationlessly to the ground state.

An alternate scheme (Scheme III) also first suggested by Wu and Rice[377] is favored by Chervinsky and Oref,[379] who found curved Stern-Volmer plots for three azoalkanes. Although pressures up to 150 atm were employed, the usual inert gas in this work (helium) is at least 20 times less efficient a quencher than the azoalkane itself. Nevertheless, their plots represent a several-fold extension of the concentration range in Figure 11. Lo was suggested to be A_v^3 whereas Sh was thought to be the random A_v^1 or nonrandom A^1 or A^3 state (referred to as A_N^*). A nonrandom state is one formed immediately upon absorption of light, whereas a random state has survived long enough for the energy to be statistically distributed among the normal modes of the reacting molecule. In this model, Sh is not subject to deactivation; that is, it only decomposes or goes to A_v^3.

A distinction has been made between curvature observed in the high-pressure region (>1 atm) and that observed in the low-pressure region.[375,380] This difference, which is quite convincing for azoethane, implies the existence of three dissociating species. Although a mathematical treatment of Stern-Volmer plots[378] shows that both Schemes II and III are capable of explaining the curvature in one region or the other, neither scheme is adequate for two different regions of curvature. Furthermore, neither mechanism includes cis-trans isomerization, which ought to take place concurrently with decomposition. The presence of *cis*-azoalkane complicates matters considerably

SCHEME IV
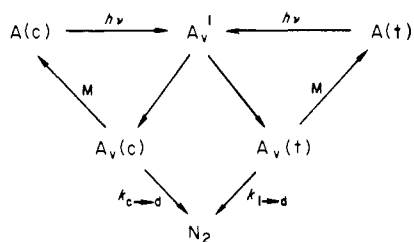
because it is more reactive than trans.

Fogel and Steel have examined the photochemistry of AIP in great detail;[90] in fact, this is the only study in which both decomposition and isomerization were monitored. Their principal findings are as follows: (1) Higher pressure or longer wavelength decreases decomposition and increases isomerization and return to starting material. (2) The Stern–Volmer plots are nonlinear (cf. Figure 11). (3) Buildup of trans (A(t)) occurs at lower pressure than does buildup of cis (A(c)). (4) In the high-pressure limit, $\Phi_{t \to c} \sim \Phi_{c \to t} \sim 0.5$. (5) Photoisomerization in solution is temperature independent. These facts, which are quite inconsistent with Scheme II, were rationalized in terms of Scheme IV.[90]

Irradiation of either isomer produces a common vibrationally excited singlet, A_v^1, which populates vibrationally excited cis and trans ground states ($A_v(c)$ and $A_v(t)$) with nearly equal probability. Theoretical calculations[115] support the idea that A(c) and A(t) share a common $^1(n,\pi^*)$ state. The hot ground states may then decompose or be deactivated by collision with inert molecules M. Higher pressure causes more deactivation of $A_v(c)$ and $A_v(t)$, favoring isomerization and return to starting material over decomposition. Shorter wavelength, on the other hand, produces the hot ground states with greater vibrational energy so they are more likely to decompose. The unique feature of Scheme IV is that for any irradiation wavelength, $A_v(c)$ is of higher energy content than $A_v(t)$ because ground-state cis-azoalkanes lie above trans by at least 7 kcal mol^{-1}.[27,127] With its greater energy, $A_v(c)$ has a faster rate of unimolecular decomposition and is less easily deactivated than $A_v(t)$. Not only should the Stern–Volmer plots curve, but the trans isomer should build up at lower pressure than the cis isomer. At very high pressures or in solution, the only reaction will be cis–trans isomerization which proceeds with a quantum yield of 0.5 because A_v^1 encounters no barrier as it partitions equally between $A_v(c)$ and $A_v(t)$.

The effect of irradiation wavelength on decomposition quantum yield makes it clear that the energy content of the decomposing species determines the rate at which it loses nitrogen. Using RRKM theory, Fogel and Steel[90] showed that the calculated rate constants ($k_{c \to d}$ and $k_{t \to d}$) for decomposition of the vibrationally excited ground states were in reasonable accord with experimental values. Wavelength effects have also been observed in the photolysis of azoethane where a change from 3519 to 3776 Å increased the lifetime of the activated molecules from 0.16 to 0.39 ns.[374] Because azoethane has fewer vibrational degrees of freedom than AIP, the lifetime in the latter case is about two orders of magnitude longer (50 ns for trans-AIP at 3655 Å). An extreme case is found in gaseous azomethane, which dissociates with unit efficiency even under 45 atm of CO_2; hence, its longest-lived dissociative state survives for less than 0.025 ns.[379]

Closely related to the wavelength effect is the long-known effect of temperature on the azoalkane decomposition quantum yield.[373,375,376,381] The enhanced Φ_r at elevated temperatures has been taken to mean that the dissociating state must surmount an activation barrier before losing nitrogen.[368,375] Provided that this state is vibrationally equilibrated, a plot of ln k_r vs. T^{-1} gives the activation energy (E_a) for dissociation (typically <5 kcal mol^{-1}). However, it has been pointed out recently[379] that raising

the temperature increases the average energy of ground-state molecules, which then have a faster rate of unimolecular dissociation once they absorb light. If the excited state dissociates prior to vibrational equilibration with the surroundings, the E_a deduced from Arrhenius plots is not the barrier height; in fact, the complex dependence of k_r on temperature[90] would not lead one to expect linear plots. Since wavelength effects support dissociation from a nonequilibrated state, the observed linearity of some Arrhenius plots[368] may be accidental. Moreover, thermolysis of photochemically produced cis-azoalkane was probable at higher temperatures in the early work, making straight lines all the more surprising. It is difficult to understand how a plot[376] of log Φ_r vs. T^{-1} can give a meaningful E_a when Φ_r is a nonlinear function of k_r [$\Phi_r = k_r/(k_r + k_d)$].

Whereas the schemes presented thus far have considerable merit, no single one of them can explain all of the data for acyclic azoalkanes. What began as a simple photolysis reaction is now rather complex because the various dissociating species might be (a) cis or trans, (b) singlet, two different triplets, or ground state, (c) vibrationally excited or equilibrated, and (d) random or nonrandom. We can come closer to a general mechanism, however, by examining the solution-phase and triplet-sensitized irradiation of azoalkanes.

c. Residual Direct Photolysis

As seen in Table XII, photolysis of acyclic azoalkanes in solution gives nitrogen with Φ_r up to about 0.5. The compounds at the upper end of this range are ones which photoisomerize to thermally labile cis isomers. On the other hand, several azoalkanes exhibit a nonzero Φ_r even though their cis isomers are completely stable at the temperature employed. Some examples are AIP ($\Phi_r = 0.02$ at 25 °C in isooctane)[90] and **179** ($\Phi_r = 0.08$ at -80 °C in toluene).[382] The inefficient photolysis

179
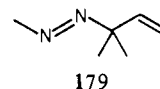
of azoalkanes in solution which does not proceed from the cis isomer will be referred to as residual direct photolysis (RDP). Any acceptable mechanism for azoalkane photochemistry must account for this process.

Pritchard et al.[375] suggest that RDP arises from pressure-independent decomposition of the vibrationally equilibrated triplet state (A_0^3 in Scheme II). As (weak) supportive evidence, they note that biacetyl can sensitize decomposition of azoethane in the gas phase. Chervinsky and Oref,[379] on the other hand, attribute RDP to the unquenchable A_N^* state in Scheme III. They discount the importance of A_N^3 because their linear Stern–Volmer plot for azoethane up to 1 atm implies that the rate constant for decay of A_0^3 would have to exceed 10^{11} s^{-1}. As already mentioned, however, the azoethane plot is actually curved in the low-pressure region.[375,380] Moreover, it is clear from results to be discussed below that triplet azoalkanes are capable of very rapid decay. Calvert et al.[335] had earlier suggested that azoalkane photolysis, including RDP, proceeds via the A_v^3, whereas Fogel and Steel[90] did not comment on RDP.

Recent solution-phase studies cast considerable doubt on the idea that A_0^3 is responsible for RDP. This process in azomethane (AM), for example, was shown by low-field CIDNP to occur predominantly from the singlet state.[383] Another study of AM in benzene revealed that Φ_r for the trans isomer (0.089) is ten times higher than for the cis isomer.[389] If A_0^3 were the decomposing species, $A_0^3(t)$ would have to lose nitrogen more efficiently than the higher energy $A_0^3(c)$. The further discovery[369] that Φ_r for AIP increases at shorter wavelength indicates that the dissociating species is not vibrationally equilibrated. Finally, the cage effect for triplet-sensitized decomposition of **179** (see structure above) is lower than that for direct photolysis at the

TABLE XII. Quantum Yields for Photolysis of Azoalkanes in Solution

compd	solvent[a]	sensitizer[b]	$\Phi_r{}^c$	ref
azomethane	AM	i		0.17	82
		h	0.15	384
		t	0.088	384
		b	0.089	369
		H_2O	0.01	82
		b	B	0.009	384
		i	A	<0.001	90
azoethane	2	hp		0.021^d	391
azo-n-propane	4			0.007	5
azoisopropane	AIP	i		0.021	90
		i		0.025^e	471
		H_2O		0	90
		c	A	<0.001	90
		m	B	v/small	90
$ClMe_2CN{=}NCMe_2Cl$	6	b		0.01	225
$NCMe_2CN{=}NCMe_2CN$	10	b		0.44	382, f
		b	B	0.10	382
		b	p-MAP	0.14	382
$Me_3CN{=}NCMe_3$	ATB	b		0.46	384
		b	B	0.02	382
		b	p-MAP	0.021	382
$MeOMe_2CN{=}NCMe_2OMe$	11	b		0.21	g
$MeSMe_2CN{=}NCMe_2SMe$	12	b		0.38	g
$HC{\equiv}CMe_2CN{=}NCMe_2C{\equiv}CH$	16	b		0.47	5
$H_2C{=}CHMe_2CN{=}NCMe_2CH{=}CH_2$	17	b		0.57	382
		b	B	0.11	382
		b	p-MAP	0.13	382
$AcOMe_2CN{=}NCMe_2OAc$	22	b		0.005	225
		nba		0.004	h
$EtOOCMe_2CN{=}NCMe_2COOEt$	35	b		0.42	420
		b	B	0.06	420
azo-1-norbornane	42	t		<0.0008	99
$PhCH_2N{=}NCH_2Ph$	48	b		0.02	g
		i		0.049	i
$PhMeHCN{=}NCHMePh$	64	i		0.035	i
		b		0.043	g
		b	B	0.025	i
$PhMe_2CN{=}NCMe_2Ph$	91	b		0.36	5
$PhCH_2MeClCN{=}NCClMeCH_2Ph$	516	b		0.1^j	397
		b	B	<0.01	397
$PhMeAcOCN{=}NCOAcMePh$	517	b		>0.26	397
		b	B	0	397
azo-1-bicyclo[2.2.2]octane	61	h		$\sim0.05^k$	98
azo-1-adamantane	112	t		$\sim0.25^k$	98
azo-$tert$-octane	56	b		0.45	g
$MeN{=}NCMe_2CH{=}CH_2$	179	t		0.47	382
		b	B	0.10	382
		b	p-MAP	0.12	382
$Me_3CN{=}NCMe_2CH{=}CH_2$	188	b		0.49	g
$Me_3CN{=}NCMe_2CH_2CMe_3$	195	b		0.42	i
tetramethyldiazetine	228	b		0.52	99
	256	p		0.36	457
3,3,5,5-tetramethyl-1-pyrazoline	229	b		0.98	99
		b	B	0.21	i
4-isopropylidene-3,3,5,5-tetramethyl-1-pyrazoline	296	b		0.45	225
		b	B	0.08	i
3-chloro-3,5,5-trimethyl-1-pyrazoline	518	b		0.12	225
3-acetoxy-3,5,5-trimethyl-1-pyrazoline	519	b		0.44	225
3-carbomethoxy-3,5,5-trimethyl-1-pyrazoline	280	b		0.86	225
4-keto-3,3,5,5-tetramethyl-1-pyrazoline	291	b		0.012	225
3-hydroxymethyl-3,5,5-trimethyl-1-pyrazoline	520	b		0.50	225
3,4-dimethyl-3,4-dicarbomethoxy-1-pyrazoline	521	b		0.52	225
	522	p		0.75	213
1,2-diazacyclohex-1-ene	425	e		0.008	g
3,3,6,6-tetramethyl-1,2-diazacyclohex-1-ene	230	b		0.008	99
		nba		0.0085	455
3,6-dimethyl-3,6-dicyano-1,2-diazacyclohex-1-ene	319	ea		0.2	455
	523	ea		0.2	455

TABLE XII (Continued)

compd		solvent[a]	sensitizer[b]	$\Phi_r{}^c$	ref
2,3-diazabicyclo[2.2.1]hept-2-ene	DBH			1.0	l
			B	0.97	355
7-isopropylidene-2,3-diazabicyclo[2.2.1]-hept-2-ene	448	m		0.95	297
2,3-diazabicyclo[2.2.2]octane	DBO	i		0.022^e	471
		i	B	0.014^e	471
1,4-dimethyl-2,3-diazabicyclo[2.2.2]octane	231	b		0.014	5
		nba		0.0065	455
1-vinyl-2,3-diazabicyclo[2.2.2]octene	466	b		0.9	455
5,6-dimethylene-2,3-diazabicyclo[2.2.2]-octene	458	b		0.8	455
	471	h		0.54	336
	472	h		0.44	457
	475	ea		0.9	455
	476	b		0.3	455
		h		0.20	336
	477	b		0.3	455
	524	ip		0.91^e	460
		ip	B	0.64^e	460
	525	d		0.98	460
		d	m-MAP	0.63	460
	514	h		0.01	336

[a] a = acetonitrile, b = benzene, c = cyclohexane, d = dichloromethane, e = ether, ea = ethyl acetate, h = hexane, hp = heptane, i = isooctane, ip = isopentane, m = methanol, nba = n-butyl acetate, p = pentane, t = toluene. [b] A = acetophenone, B = benzophenone, p-MAP = p-methoxyacetophenone. [c] Nitrogen quantum yield unless designated otherwise. [d] At 0 °C. [e] Quantum yield of hydrocarbon formation. [f] Back, R.; Sivetz, C. Can. J. Chem. 1954, 32, 1061. Smith, P.; Rosenburg, A. J. Am. Chem. Soc. 1959, 81, 2037. [g] Bishop, D. J. unpublished results. [h] Nalepa, C. J. unpublished results. [i] Engel, P. S. unpublished results. [j] Photoracemization; see IV.A.3. [k] Depends on solvent and temperature; cf. II.A.4. [l] Steel, C. J. Phys. Chem. 1963, 67, 1779.

SCHEME V

A(c) $\xrightarrow{h\nu}$ A$_N^1$(c) $\longrightarrow$ A$_v^1$ $\longleftarrow$ A$_N^1$(t) $\xrightarrow{h\nu}$ A(t)

SCHEME VI

A(c) $\underset{M}{\overset{h\nu}{\rightleftharpoons}}$ A$_v^1$(c) $\longrightarrow$ 2R· + N$_2$ $\longleftarrow$ A$_v^1$(t) $\underset{M}{\overset{h\nu}{\rightleftharpoons}}$ A(t)
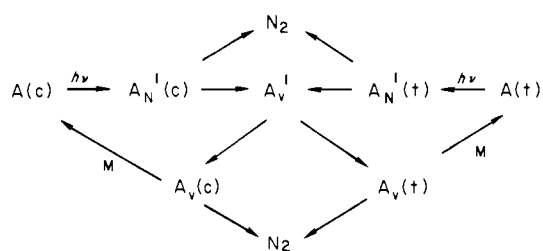
same temperature (−80 °C), implying that the major part of RDP does not involve the triplet state[382] (cf. IV.B).

If the species responsible for RDP is neither triplet nor vibrationally equilibrated, perhaps it should be identified as A$_0^1$. In this case, however, both isomers should exhibit the same Φ_r because they share a common A$_0^1$ state.[115] One remaining possibility is that cis and trans isomers each give their own nonrandom state, A$_N^1$(c) and A$_N^1$(t), which can either decompose or undergo energy randomization. A combination (Scheme V) of Fogel and Steel's mechanism[90] with Chervinsky and Oref's nonrandom moiety[379] accounts for the chemistry of AIP without invoking the triplet state. Using the classical model of unimolecular decomposition, Zimmerman et al.[369] were unable to correlate the wavelength dependence of Φ_r for RDP of AIP with dissociation from A$_v^0$, A$_v^1$, or A$_v^3$. This may be taken as support for the intermediacy in Scheme V of A$_N^1$, for which the as-

sumptions of unimolecular reaction theory break down. The decrease in the quantum yield of RDP in polar solvents could be due to an increase in the effective size of the azoalkane by association with such solvents.[5,336] If RDP arises from an energy-localized $^1(n,\pi^*)$ state, as seems likely, solvation of the azo groups must aid conversion to the energy-randomized species. The higher Φ_r of trans-AM than cis-AM can be rationalized as greater solvation of the more polar cis isomer, thus facilitating energy randomization and deactivation.[389]
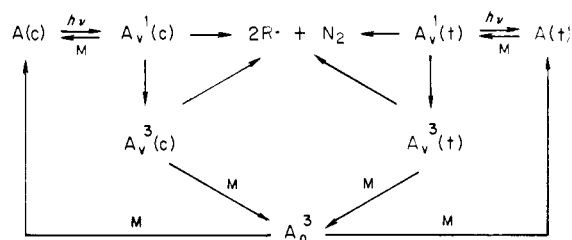
Although residual direct photolysis is fairly common, it is not ubiquitous. Thus Φ_r for azo-1-norbornane (42) is less than 0.0008[99] and cumylazo-1-norbornane (219) maintains an isosbestic point on irradiation at −120 °C,[70] signifying the absence of RDP. In view of the fact that both AM and α,α-dimethylallylazomethane (179)[382] exhibit moderately efficient RDP, alkyl group size may be the determining factor.

Scheme VI shows another proposed mechanism for the photolysis of AM.[369] RDP would have to arise from $A_v{}^1(t)$ but not from $A_v{}^1(c)$ in order to explain the higher Φ_r for the trans than the cis isomer. Part of the experimental support for Scheme VI is that the quantum yield for direct photoisomerization ($\Phi_{t \to c}$ = 0.42)[369] agrees with that reported[384] for the benzophenone-sensitized reaction ($\Phi_{t \to c}$ > 0.4). Both modes of excitation might populate $A_0{}^3$, which partitions between cis and trans ground states. However, the sensitization result has been questioned by Fogel and Steel,[90] who found that acetophenone gives $\Phi_{t \to c}$ = 0.11. Whereas these workers suggest that the benzophenone value is too high on account of direct light absorption by azomethane, Zimmerman et al.[369] believe that both results are correct and that the higher energy sensitizer, acetophenone, leads to less isomerization and more decomposition, presumably via $A_v{}^3 \to N_2$. The latter explanation is very unlikely because acetone-sensitized decomposition of AM exhibits Φ_r = 0.037, not much higher than the 0.0087 value for benzophenone.[384] If high-energy sensitizers enhanced decomposition, the very energetic acetone triplets (triplet energy = E_T = 80 kcal mol^{-1}) should have given a greater Φ_r than acetophenone, whose Φ_r based on Scheme VI would be 1 - (2 × 0.11) = 0.78. Most likely the benzophenone result is indeed too high, though further investigation in this area is needed to clarify the discrepancy with the acetophenone value. Even if Scheme VI is correct for AM, it cannot be general because trans-AIP builds up at lower pressure than the cis isomer.[90] $A_0{}^3$ is a relaxed triplet state of intermediate configuration which should lead to the same cis–trans ratio regardless of pressure. Although Scheme V is the best mechanism presented thus far, we shall see in the next section that it is not the only one which explains the results.

2. The Triplet State

Examination of the various models for azoalkane photochemistry reveals that the role of the lowest triplet state is a center of controversy. Under what circumstances do azoalkanes intersystem cross and what is the fate of the triplet? Since no phosphorescence has been observed from any azoalkane, these questions have been approached by indirect means. It should be pointed out that the new techniques of optoacoustic spectroscopy[385] and thermal lensing[386] are now available for examining radiationless processes, and these might prove useful on the azoalkane problem.

A number of reports have appeared on the gas-phase triplet-sensitized photolysis of acyclic azoalkanes, and the results through 1975 have been tabulated by Fogel and Steel.[90] More recently, the biacetyl-sensitized photolysis of azoethane was reported.[375] All of the biacetyl results[335,376,387] can be summarized as follows: azoalkanes quench biacetyl phosphorescence[351] (E_T = 55 kcal mol^{-1}), but the efficiency of sensitized decomposition, which is quite low at ambient temperatures, rises to only 0.16 at 160 °C and 29.8 torr for AIP.[376] Decomposition of the triplet state is associated with an activation energy (see above) of 5–9 kcal mol^{-1}. Sensitization by acetone is more efficient, the highest reported Φ_r being 0.52 for AM at 30 °C and 12.4 torr.[371] Although triplet-sensitized decomposition is a viable process in the gas phase, one must wonder why its efficiency never reaches the value of unity often seen in direct photolysis. In particular, if $A_v{}^3$ is to be named as the principal decomposing species at low pressures under direct irradiation (cf. Schemes II, III, VI), should the same species not decompose efficiently when produced by energy transfer from a high-energy donor? The acetone-sensitized type-II reaction of n-butyraldehyde, for example, proceeds in the gas phase with essentially the same quantum yield as for direct irradiation.[388] According to Chervinsky and Oref,[379] collision of excited donor with ground-state acceptor does not necessarily impart sufficient
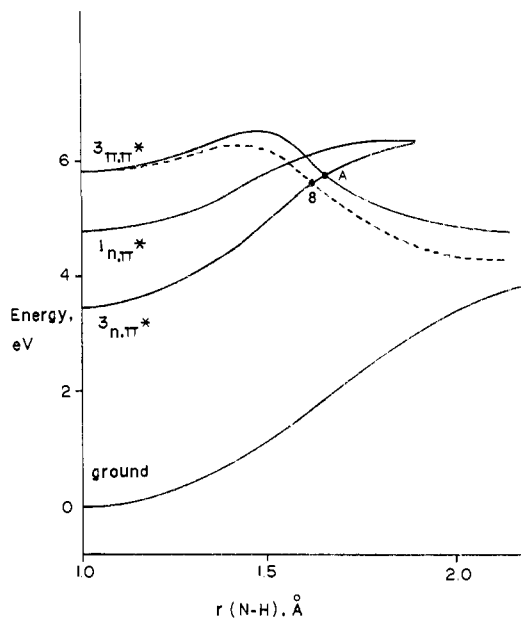

Figure 12. Calculated potential energy curves for elongation of one H—H bond of cis-diimide.[10] The dashed line shows the behavior expected for dissociation of the $^3(\pi,\pi^*)$ state to a stabilized radical.
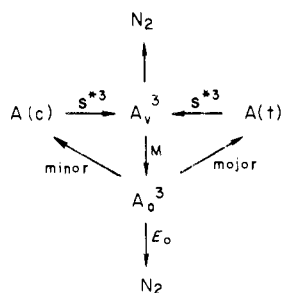
energy to the acceptor for it to react. For example Φ_r for the acetone-sensitized photolysis of AM at 13 torr is calculated to be 0.78.[379] Although this value is higher than that found experimentally (0.52),[371] it is considerably below unity. It follows from this theory that the low quantum yields for gas-phase sensitized photolysis of azoalkanes cannot be used as evidence against the intermediacy of triplets in direct irradiation. Of course the existence of triplet-sensitized decomposition, even when efficient, cannot be taken as proof that direct photolysis also proceeds via the triplet state. A further problem in obtaining useful information from gas-phase sensitized photolyses is dissociation of the sensitizers to a variety of free radicals which can enter into secondary reactions.[371,375]

Until recently, triplet-sensitized decomposition of acyclic azoalkanes in solution was an unknown process. Neither AM, AIP, nor ATB exhibited a Φ_r greater than anticipated from trivial direct light absorption.[90,382,384] It is now known[382] that triplet sensitization can occur if the azoalkane is thermally labile, e.g., **10, 17, 35, 179**. The observation that Φ_r does not exceed 0.14

10   **17**

35
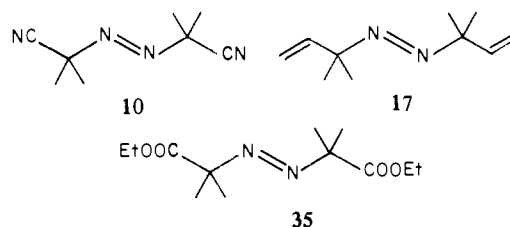
regardless of sensitizer E_T suggests decomposition from a vibrationally equilibrated state, $A_0{}^3$. In accord with this idea, E_a for **179** was only 1.5 kcal mol^{-1}, compared to the 5–9 kcal mol^{-1} reported for more thermally stable azoalkanes in the gas phase.[375,376] A recent theoretical calculation on diimide[110] suggests an explanation for the relation between thermal lability and Φ_r. As shown in Figure 12, decomposition occurs when the $^3(n,\pi^*)$ state acquires sufficient energy to cross the dissociative $^3(\pi,\pi^*)$ curve at point A. When the azoalkane is more labile, the dissociative curve should lie lower, as in the dashed line. The new crossing point, B, is now more accessible so that dissociation can compete better with radiationless decay. The identical values of Φ_r for **17** and **179** under triplet sensitization support the one-bond scission shown in Figure 12; further discussion of this point is deferred to section IV.B.

SCHEME VII

$$N_2$$
$$\uparrow$$
$$A(c) \xrightarrow{S^{*3}} A_v^3 \xleftarrow{S^{*3}} A(t)$$
minor $\searrow$ $\downarrow M$ $\swarrow$ major
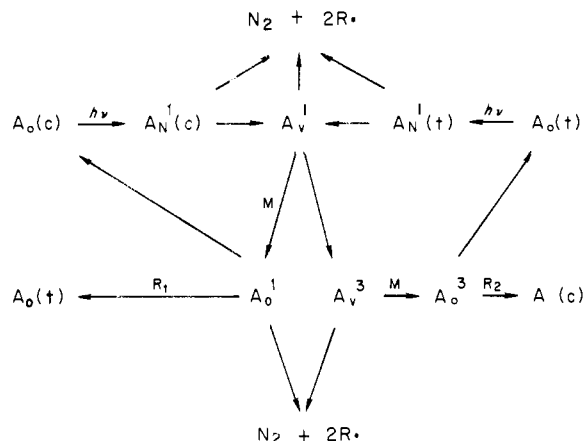$$A_o^3$$
$$\downarrow \varepsilon_o$$
$$N_2$$

Triplet-sensitized isomerization of acyclic azoalkanes in solution has received some attention, but the corresponding gas-phase reaction is virtually unknown. Solution-phase quantum yields for the trans → cis reaction in simple azoalkanes range from 0.04 to 0.11.[90] That ATB does not undergo sensitized trans → cis isomerization is proven by the low (<0.02) sensitized Φ_r at ambient temperatures; any cis isomer which formed would have given nitrogen. The possibility that the moderate Φ_r (0.12) for the acetophenone-sensitized decomposition of **179** is due to prior trans → cis isomerization was discounted by low-temperature NMR and nitrogen evolution experiments.[382]

In contrast to the small $\Phi_{t \to c}$ values, $\Phi_{c \to t}$ for AIP sensitized by benzophenone is 0.70.[90] The remarkably high efficiency of this process raises several questions: (a) Why is the sum of $\Phi_{t \to c}$ and $\Phi_{c \to t}$ less than unity (0.74 ± 0.05) when T_1 is supposed to have no barrier to isomerization?[114-116,120] (b) Do any azoalkanes besides AIP exhibit the same behavior? (c) Is there a connection between the high value of $\Phi_{c \to t}$ and the fact that the cis → trans reaction is exothermic? (d) Does a steric factor favor formation of the cis donor–acceptor complex?[379] Although no answer to (a) is presently available, it is known with regard to (b) that benzophenone or thioxanthone isomerizes cis-azo-1-norbornane (**42c**) with quantum yields of 0.87 and 0.77, respectively.[98] Question c is raised because other photoisomerizations which proceed only in the exothermic direction have been attributed to chemical interaction between sensitizer and olefin.[389] However, the near-diffusion-controlled quenching rate constant for acetophenone triplets by AIP[90] and the high efficiency of $^3(\pi,\pi^*)$ thioxanthone as sensitizer for **42c** speak against this mechanism. Finally, the steric factor mentioned in (d) does exist, but energy transfer to the cis isomer is probably no more than 2.5 times faster than to the trans isomer.[90,351]

It is clear from the above results that the ratio $\Phi_{c \to t}/\Phi_{t \to c}$ and the decay ratio[389] are much greater for triplet-sensitized irradiation than for direct photoisomerization. This key observation means that the isomerization seen on direct irradiation is unlikely to proceed via the triplet manifold, in accord with Scheme V but not Scheme VI.[90] Nevertheless even this conclusion has been disputed, for Chervinsky and Oref[379] invoke both the above-mentioned steric factor and a reaction coordinate in which azoalkane inverts as the ground-state sensitizer leaves the donor–acceptor complex. Pritchard et al.[380] dismiss this idea, noting that singlet sensitizers play no role in directing the course of azoalkane isomerization. On the other hand, Camp et al.[115] have suggested, on the basis of theoretical calculations, that the isomerization quantum yields may depend upon whether T_1 was populated by triplet sensitization or by intersystem crossing (ISC). In my opinion, the clear-cut difference of decay ratios is most simply interpreted if direct irradiation does not populate A_o^3 in solution.

On the basis of the foregoing discussion, Scheme VII is presented to rationalize the data for triplet-sensitized irradiation of acyclic azoalkanes. A_v^3 represents the $^3(n,\pi^*)$ state, which is common to both isomers.[114,115] Isomerization is the major channel unless one of the C–N bonds is weak or irradiation is carried out with a high-energy sensitizer or at elevated tem-

SCHEME VIII

$$N_2 + 2R\cdot$$

$$A_o(c) \xrightarrow{h\nu} A_N^1(c) \longrightarrow A_v^1 \longleftarrow A_N^1(t) \xleftarrow{h\nu} A_o(t)$$

$$M$$

$$A_o(t) \xleftarrow{R_1} A_o^1 \qquad A_v^3 \xrightarrow{M} A_o^3 \xrightarrow{R_2} A(c)$$

$$N_2 + 2R\cdot$$

perature in the gas phase. Taken together, Schemes V and VII explain azoalkane photolysis rather well without invoking ISC at all.

Pritchard, Marchant, and Steel[380] have recently set forth another general mechanism for azoalkane photochemistry. As shown in Scheme VIII, these authors propose that A_v^1 is deactivated to A_o^1 in solution but that it intersystem crosses to A_v^3 in the gas phase. The latter process is facilitated as A_v^1 explores its whole energy surface, whereas collisional deactivation forces this singlet state to exist in a region close to the ground-state surface. The different decay ratios for direct (R_1) vs. sensitized (R_2) irradiation are characteristic of the two electronic states involved. The key experiment which led to dissatisfaction with Scheme V was that Φ_r for AIP tended toward unity at high pressure and temperature. Whereas this result is rationalized in Scheme VIII as decomposition of A_o^1, the only source of decomposition expected from Scheme V under these conditions is thermolysis of the cis isomer, which is produced with a quantum yield of only about 0.5. However, decomposition of A_N^1 may not be minor at elevated temperatures; witness the large dependence of Φ_r on temperature for AM[390] and azoethane[391] under conditions where all decomposition probably arises from A_N^1.

Despite the large amount of work described above, the question of whether azoalkanes intersystem cross remains unanswered. However, some information about the elusive triplet state is provided by MO calculations. Four calculations[120,129,136,138] showed the $^3(\pi,\pi^*)$ state lying considerably above the $^1(n,\pi^*)$ state, thus excluding the former from participation in ordinary azoalkane photochemistry. ISC from $^1(n,\pi^*)$ to $^3(n,\pi^*)$ was expected to be slow,[355] a conclusion reinforced by the large magnitude of the singlet–triplet energy gap (~20 kcal mol⁻¹). However, two other calculations[114,115] located $^3(\pi,\pi^*)$ below $^1(n,\pi^*)$, with the two states crossing or nearly touching at some geometries. This result suggests that the observed[352] triplet state at 63.4 kcal mol⁻¹ might be $^3(\pi,\pi^*)$, with the $^3(n,\pi^*)$ state being missed.[90] If this suggestion is correct, the triplet band[352] at 111 kcal mol⁻¹ is left unassigned. Moreover, the rapid decline in energy-transfer rate constants[351] with sensitizers below 55 kcal mol⁻¹ would require that T_1 (the $^3(n,\pi^*)$ state) not be accessible by energy transfer. The possibility that the two triplet states lie below the lowest singlet state in azoalkanes raises the question whether one triplet is reached by sensitization and the other by ISC. However, studies of the spin-correlation effect to be discussed below tend to discount involvement of any triplet in solution-phase direct photolysis. It is also tempting to attribute direct photoisomerization to one triplet state and photosentized isomerization to the other, but two MO calculations[114,138] show a high barrier to this process for the $^3(\pi,\pi^*)$ state. The rarity of T_2 photoreactions[392] and the absence of any data which demand participation by two triplet

states suggest that T_2 serve only as a vehicle to facilitate ISC, if ISC is to be invoked at all.

3. Other Photochemical Studies

Although only thermally labile acyclic azoalkanes are subject to triplet-sensitized decomposition, all of them can be excited by singlet sensitization. Thus irradiation of naphthalene at 254 nm in the presence of AIP produces a larger steady-state concentration of cis-AIP than direct irradiation would.[393] This synthetically useful device replaces the unfavorable direct excitation ratio [ε(cis) ≫ ε(trans)] with equal diffusion-controlled singlet-energy-transfer rate constants to the two isomers. The unique absorption spectra of azoalkanes, which show a window in the region of 280 nm (cf. III), invited a study of singlet-energy-transfer rate constants.[394] As predicted by theory, these rates fall off not only when the energy of the donor is too low but also when it is too high.[5]

A quantitative study[384] of ATB in the presence of excited triphenylene revealed behavior not expected for ordinary singlet energy transfer. Whereas a plot of Φ_r^{-1} vs. $[A]^{-1}$ would normally be linear with a slope equal to k_d/k_t (k_d = rate constant for sensitizer singlet decay, k_t = rate constant for energy transfer to azoalkane (A)), the plot in this case curved upward, suggesting that Φ_r is abnormally low at small $[A]$. A possible explanation is based on the observation discussed above that cis-azoalkanes revert efficiently to the trans isomers under triplet sensitization. Since fewer triphenylene singlets are quenched when $[A]$ is small, more of the excited triphenylene can intersystem cross. The resulting triplets sensitize reversion of cis-ATB to trans-ATB, whereas the cis isomer normally would have given nitrogen. Consideration of the kinetics of this process shows that a term $[A]^2$ is introduced into the usual Φ_r^{-1} vs. $[A]^{-1}$ plot, in accord with the observed curvature. This explanation is untested.

Another anomaly appears in Table XII when comparing Φ_r for azotoluene derivatives. Whereas a high value is found for azocumene, Φ_r for azotoluene and azo-α-phenylethane is quite small. Either the latter two compounds do not form the cis isomers photochemically or else the cis isomers fail to give nitrogen. Hydrazone formation probably intervenes in this reaction, judging from the report[67] that **526** is converted to **527** on irradiation. The tendency of cis-azoalkanes to tautomerize


526   527
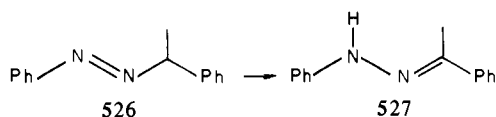
in the presence of acid or base, the reactivity of hydrazones toward oxygen, and formation of UV-absorbing products[395] have prevented mechanistic clarification of the low Φ_r for azotoluenes. It should be noted that the UV-absorbing hydrocarbons first observed[28] in azocumene decomposition have been found[395] to consist of α-o-cumyl dimers as well as the α-p dimers initially proposed.

As seen in Table XII, α-chloro- and α-acetoxyazoalkanes **6** and **22** also lose nitrogen very inefficiently. Levi and Malament[396] have discovered that compounds of this type undergo photoinversion at the α-carbon atom, as shown below. This process,

516   528
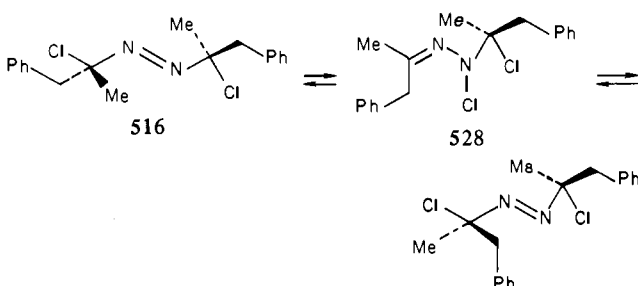
which occurs to the exclusion of isomerization and residual direct photolysis, is thought to involve a hydrazone intermediate (**528**). In the case of α,α'-dipropionoxyazoalkanes, irradiation in the presence of acetic acid leads to photosubstitution as well as photoinversion via ion pair **529**. More recently, it was re-


529
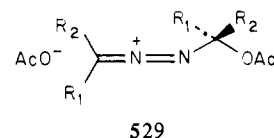
ported[397] that photoinversion via **528** proceeds with a quantum yield of 0.1 whereas photosubstitution via **529** exhibits $\Phi = 0.34$. When the phenyl group was directly attached to the α-carbon atom, normal azoalkane fragmentation became competitive with C–Cl cleavage in **530** and was the exclusive pathway in **517**

530   517
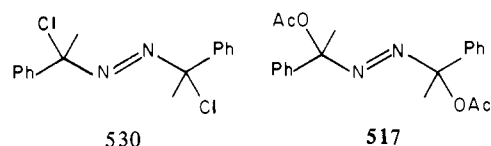
($\Phi_r > 0.26$). Although these reactions were shown not to proceed under triplet sensitization, the possible intermediacy of cis isomers remains untested.

A clever method for replacing amino groups with trifluoromethyl groups is based on photolysis of the azoalkane, as shown below.[398] Unfortunately, this sequence is not likely to be useful

$$RNH_2 \xrightarrow{CF_3NO} RN{=\!\!=}NCF_3 \xrightarrow{h\nu} RCF_3$$
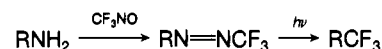
for groups other than CF_3 as neither the condensation step nor residual direct photolysis is a general reaction.

Photolysis of azoalkanes in the solid state has produced several interesting results; for example, disproportionation accounts for only 5% of the radical–radical reactions of 2-cyanopropyl in fluid solution but for 95% in the crystal.[399,400] The cage effect in crystalline AIBN (**10**) is greater than 91%.[401] Perhaps the most fascinating result in this area is the persistence of triplet radical pairs from low-temperature matrix photolysis of **531**.[402]

531
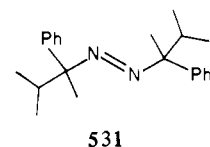
B. Spin Correlation Effects

A radical pair which gives different products depending upon its multiplicity is said to exhibit a spin correlation effect (SCE). Because loss of nitrogen provides an appealing method of producing radical pairs, azo compounds have found considerable use in studying SCE's. For example, Bartlett and Porter decomposed the cyclic azo compound **323** by direct photolysis ($h\nu$) and by triplet sensitization (S^{*3}), as shown in Scheme IX.[251] Conservation of electron spin[403] predicts that loss of ground-state nitrogen will produce diradicals of the same multiplicity as their electronically excited precursor. Since interaction of two species having the same electron spin quantum number leads to a repulsive potential curve, the triplet diradical (R↑↑R) cannot recombine to form a cyclobutane until spin inversion has occurred. If (R↑↑R) can undergo a geometric change which is fast enough to compete with spin inversion, it might be diverted to a new triplet biradical (R↑↑R'), in this case a rotamer of the original biradical. (R↑↑R') eventually relaxes to (R↑↓R') which recombines freely to give the cyclobutane of opposite stereochemistry from that of **323**. In fact **323** did exhibit a SCE, for

SCHEME IX
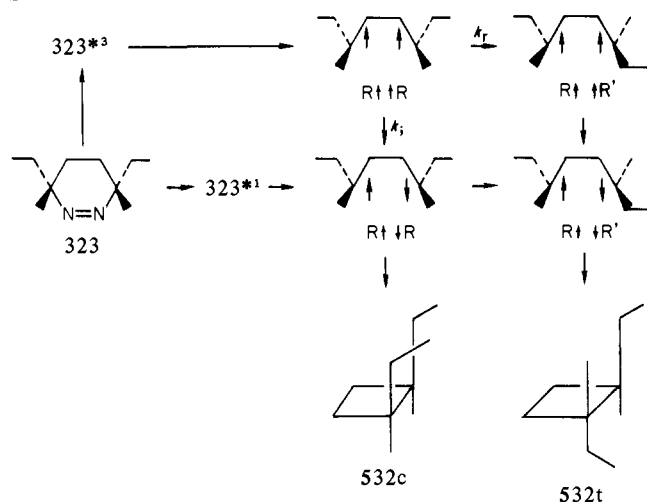
the ratio of **532c** to **532t** fell from 10.0:1 under direct irradiation to 1.4:1 under triplet sensitization. Thus (R↑↓R) mainly recombined, but the products of sensitized photolysis were characteristic of a nearly equilibrated mixture of (R↑↑R) and R↑↑R').

Stephenson and Brauman[252] have questioned this interpretation of the results on **323**. In their view, predominant loss of stereochemistry in (R↑↑R) implies that the bond rotation rate constant (k_r), estimated to be 10^6–10^8 s^{-1}, exceeds the rate of spin inversion (k_i) by a factor of 10^2. With a k_i value of only 10^4–10^6 s^{-1}, the triplet diradicals would have a lifetime of 10^{-4}–10^{-6} s, longer than they felt was intuitively reasonable. Stephenson and Brauman suggested that SCE's arose because the vibrationally excited triplet diradical produced by photosensitized decomposition is deactivated and intersystem crosses to a singlet diradical which mostly loses stereochemistry. Thermolysis or direct irradiation, on the other hand, was said to generate vibrationally excited singlet diradicals which could readily overcome the barrier to stereospecific closure.

This alternate interpretation of SCE's has met with considerable opposition,[404] and the arguments have been nicely summarized by Bergman.[191] Retention of stereochemistry under direct irradiation means that the barrier to rotation exceeds that for ring closure, but the latter barriers are probably lower than the 5–8 kcal mol^{-1} originally expected.[221] Recently, several research groups[405–407] have succeeded in trapping triplet 1,4-diradicals from ketone photolysis and found that their lifetimes are indeed as long as 10^{-4} s. Spin inversion in the triplet diradicals was held to be the rate-determining step in their disappearance,[407] in support of the Bartlett–Porter interpretation of SCE's.

SCE's have been reported for many cyclic and bicyclic azoalkanes, as shown by the examples below. In each case, the competition between some molecular motion and spin inversion gives rise to a different product distribution in direct vs. triplet-sensitized photolysis.

Although cyclic azoalkane studies have become more popular, the first azoalkane experiment involving a SCE was carried out in the acyclic series. By photolyzing azomethane in a high-density propane gas, Lyon[418] deduced a rate of methyl radical recombination of 10.2 × 10^{13} cm^3 mol^{-1} s^{-1}. This value is four times higher than that obtained by using a low-pressure gas.[419] The explanation given is that in the latter case, randomly oriented methyl radical spins allow recombination on one out of four collisions. On the other hand, radicals produced in the high-density gas come from the same singlet precursor and hence do not have this restriction. Note that this result speaks against azomethane intersystem crossing in the high-density gas since decomposition from the triplet state would give radicals with the lower recombination rate.
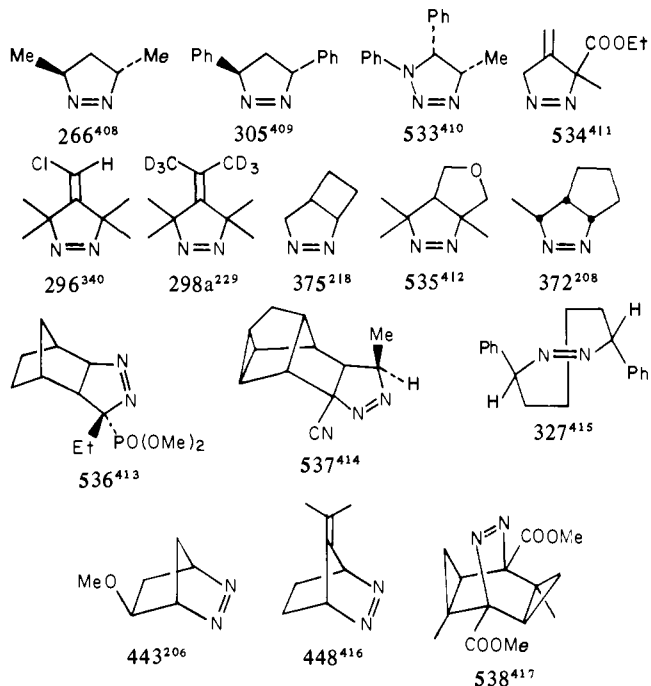
In the first solution-phase SCE study, Fox and Hammond[420] produced cyanocyclohexyl radicals by photolysis of azo-1-cyanocyclohexane (**54**) and its related ketenimine **539**. Instead
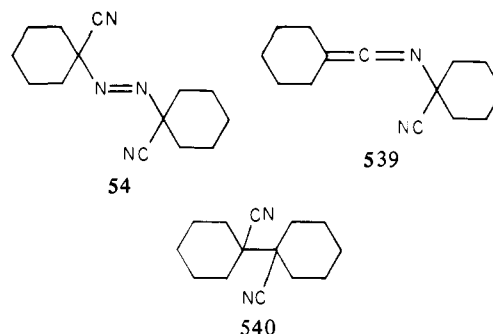
of rotation about a single bond as in **323**, the process competing with radical combination was diffusion of cyanocyclohexyl radicals from the solvent cage[421,422] followed by their reaction with cumene solvent. Ketenimine **539** showed a SCE in that more triplet radical pairs escaped the cage than singlet pairs. Since spin inversion was relatively slow, the barrier to recombination in the triplet pairs allowed more of them to escape. Azo compound **54**, on the other hand, showed virtually no SCE, the percentage cage recombination (cage effect) being 19.9 and 17.7% for direct and sensitized irradiation, respectively. It was later found[384] that the supposed triplet sensitizers used by Fox and Hammond were capable of transferring singlet energy to the azo compound (see above). Whereas the ketenimine results may be valid, those with **54** are in doubt because direct and sensitized photolysis both produced singlet radical pairs. Other studies[423,424] which employed aromatic hydrocarbon sensitizers are likewise of dubious value in deciding whether a SCE can be observed in acyclic azoalkanes.

Closer examination of Fox and Hammond's results reveals that singlet sensitization does not explain their failure to observe a SCE. From their concentration of **54** (10^{-4} M), the singlet lifetime of triphenylene (37 ns),[425] and a reasonable value of k_q (6 × 10^9),[351] one can calculate that only 2% of the sensitizer singlets were quenched by **54**. Triphenylene triplets, on the other hand, are sufficiently long-lived (0.625 ms)[426] that they should transfer energy to **54** with 95% efficiency under these conditions. Triplet-sensitized photolysis is only one-fourth as efficient as direct (cf. IV.A.2), but even this factor will not significantly

TABLE XIII. Cage Effects for Decomposition of 17

| mode of decomposition	cage effect
thermolysis at 54 °C	0.44
direct photolysis	0.61
acetophenone sensitized	0.09
p-methoxyacetophenone sensitized	0.13
thioxanthone sensitized	0.07

SCHEME X
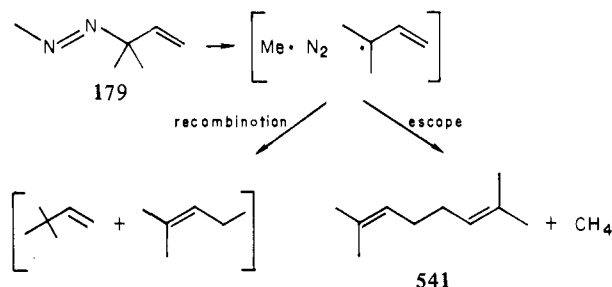
reduce the fraction of **54** decomposing via the triplet state.

An apparent solution to the problem of singlet sensitization (which surely occurred in at least one SCE study)[423] would be to employ an aromatic ketone sensitizer which would intersystem cross so rapidly as to preclude the transfer of singlet energy. Although Fox and Hammond[420] measured Φ_r for decomposition of **35** sensitized by several aromatic ketones, none of these sensitizers was employed in the cage-effect study, probably because they decomposed **54** much less efficiently than did triphenylene. Later work[382] showed that aromatic ketones are perfectly acceptable sensitizers for decomposition of AIBN (**10**) and thus presumably also of **54**. Nelsen and Bartlett[423] decided upon the aromatic hydrocarbons triphenylene and pyrene as sensitizers for azocumene (**91**) photolysis because "use of acetophenone and benzophenone in this system led to new products, probably by photoreduction of the sensitizer".[423] From the known[351,384] rate constants for energy transfer to azoalkanes and for photoreduction[427] of benzophenone by toluene, one can calculate that energy transfer to azocumene should have been at least 99% efficient. The presence of photoreduction products is therefore surprising, although the use of di-*tert*-butyl nitroxide as scavenger could have led to new products.[428] Other reports[251,340,429] have mentioned difficulties in using benzophenone to sensitize decomposition of azoalkanes, but this sensitizer works admirably in many cases.[206,355,382,408-417]

Although the reasons for failure to observe a SCE in **54** and azocumene remain obscure, the observation of a nonzero Φ_r for the triplet-sensitized photolysis of **17** and **54** suggested that the cage effect for these compounds would be a fruitful area of study. Once it was proven that triplet-sensitized photolysis did not proceed via the cis isomer, cage effects for **17** were measured[382] by isotopic labeling to avoid introducing another potential reactant into the system. As pointed out by Fox and Hammond,[420] scavengers reactive enough to capture relatively stable free radicals are unsuitable for photochemical studies. Thus the Koelsch radical, nitroxyl radicals, and iodine would nicely scavenge free dimethylallyl radicals, but these substances would also absorb light and quench sensitizer triplets, giving rise to undesired side reactions. Possible randomization of the spin of triplet radical pairs by high concentrations of stable radicals is another reason to avoid such substances.[430,431]

The results of this study of **17** are shown in Table XIII. Whereas the lower cage effect in thermolysis than direct photolysis is due only to the temperature difference,[28] triplet-sensitized irradiation showed markedly lower cage effects at the same temperature. A similar result was seen in **179**, which gave much more cage escape products under sensitized irradiation at -80 °C than under direct irradiation (Scheme X).[382] Recent

reports of SCE's in other acyclic systems[432-435] make it tempting to attribute the lower cage effects in Table XIII to the same cause; however, CIDNP studies[382] revealed unexpected complexities in the decomposition of **17**. Whereas thermolysis produced only a steady increase in the NMR peaks due to hydrocarbon recombination products (e.g., **541**) and direct irradiation gave only minor CIDNP signals, thioxanthone-sensitized photolysis produced a greatly enhanced absorption for the methyl protons of **541**. The observed polarization is consistent with decomposition to a triplet diazenyl-alkyl pair, **542**. If the diazenyl radical were to diffuse from the solvent cage before losing nitrogen, the result would be a lower apparent cage effect.
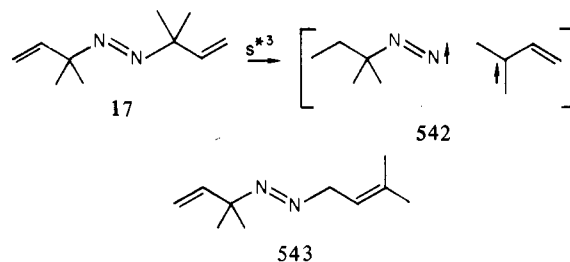
Alternately, radical pair **542** could lose N_2 in the cage, in which case the conventional SCE explanation would apply. These possibilities are not readily sorted out, though the absence of turnaround product **543** implies that no large fraction of diazenyl radicals escape the cage or that if they do, recombination with free dimethylallyl radicals competes poorly with loss of N_2.

The idea that triplet azoalkanes decompose stepwise in solution is rather surprising, but some theoretical justification is available.[110] Comparison of one-bond cleavage with concerted elongation of both N-H bonds in cis-diimide revealed that the activation energy for crossing of the $^3(n,\pi^*)$ state with the dissociating $^3(\pi,\pi^*)$ state is much lower in the stepwise mechanism (cf. Figure 12). It should be noted that the results on **17** and **179** strongly support the viewpoint that residual direct photolysis does not proceed from a triplet state of the azoalkane, contrary to the diimide calculations.[110] If triplet-sensitized photolysis of cyclic azoalkanes also proceeds stepwise, bond rotation could occur in the diazenyl radical instead of in the pair R↑↑R in Scheme IX. Evidence for the intermediacy of alkyl-diazenyl radicals in azoalkane direct photolysis is lacking, but an elegant series of experiments by Porter et al. provides overwhelming evidence for phenyldiazenyl radicals.[67]

C. Cyclic Azoalkanes

The photochemistry of diazirines has been investigated extensively and the subject was reviewed in 1966[436] and 1977.[437] These useful carbene precursors[181,178] exhibit highly structured absorption spectra[178,438] and only weak fluorescence.[338] Although no quantum yields have been reported in solution, Φ for the disappearance of diazirine itself in the gas phase is 2.[156,439] This high value has been attributed[156] to a chain reaction which is inhibited by propane (Φ = 1.1 ± 0.2)[439] and which is apparently absent in methylchlorodiazirine (Φ = 0.945 ± 0.02 at 250 and 325 nm, independent of pressure).[440]

Amrich and Bell[156] reported in 1964 that gas-phase irradiation of diazirine led in part to diazomethane, but similar experiments by Moore and Pimentel[441] did not show this product. Frey[436] has noted that the estimated heats of formation (ΔH_f) of diazirine and diazomethane (49 and 79 kcal mol^{-1}, respectively) are such that Amrich and Bell's rearrangement is highly exothermic. If formed in the ground state, the resulting diazomethane would be vibrationally excited and it would dissociate within 10^{-12} s; therefore, a significant yield of this product is not expected even at 600-mm pressure. This criticism is reinforced by another determination[442] of ΔH_f for diazomethane (51.3 kcal mol^{-1}) and a thermochemical estimate[443] of ΔH_f for diazirine (111.4 kcal

mol^{-1}). More recently, Lahmani[439] also found that irradiation of diazirine gives diazomethane, but the mechanism does not seem to be a simple photorearrangement. Not only was the yield of diazomethane unaffected by irradiation wavelength (rearrangement should be less able to compete with dissociation of diazirine at shorter wavelength), but addition of propane, a scavenger of methylene, totally suppressed diazomethane formation. The reaction

$$CH_2 + diazirine \rightarrow CH_2 + diazomethane$$

accounts for diazomethane formation and avoids the thermochemical problem[440] since part of the excess energy could be carried off by CH_2. The failure of Moore and Pimentel[441] to observe diazomethane is not readily explained, though it should be noted that this substance is prone to form azine in a thermal reaction (cf. II. C.1).[445]

Although diazirine itself seems not to rearrange directly to diazomethane, it is quite clear that substituted diazirines do undergo this reaction.[438,440,446] In aryldiazirines, for example, roughly half of the arylcarbene is derived from photolysis of the rearrangement product and the other half comes from the diazirine itself, as illustrated below. Rearrangement was not
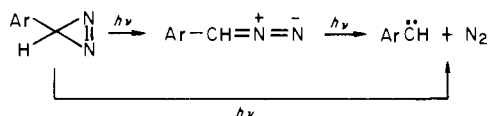

detectable on irradiation of 3-aryl-3-halogenodiazirines in solution, possibly because the resulting diazo compounds are thermally labile.[153,447] On the other hand, gas-phase photorearrangement of 3-methyl-3-chlorodiazirine (**236**, Table VIII) was required to explain the inhibiting effect of acetic acid on formation of 1,1-dichloroethane.[440]

Triplet-sensitized photolysis of diazirines has been examined only very recently, though the triplet energy of dimethyldiazirine (68 kcal mol^{-1}) has been known since 1972.[448] In the gas phase, the primary product of benzene- or pyrazine-sensitized photolysis of diazirine is triplet methylene, whereas direct irradiation produces singlet methylene.[439] Irradiation of *tert*-butyldiazirine (**544**) in the gas phase or in solution gives roughly equal amounts of **545** and **546** because rearrangement of the vibrationally excited singlet diazirine or carbene is faster than loss of energy to the surroundings. On the other hand, triplet
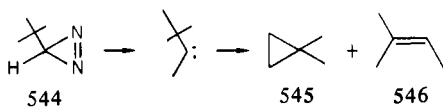

sensitization or thermolysis leads mostly to **545**, suggesting that these two decomposition modes proceed via the same intermediate. According to Chang and Shechter,[449] this intermediate is the singlet carbene produced by endothermic ISC from the triplet carbene. It follows that the singlet carbene is not much higher in energy than the triplet carbene, but the magnitude of this energy gap is controversial.[450]

The photochemical lability of larger cyclic azoalkanes is remarkably dependent upon their ring size, as shown by the quantum yields for **228–230**.[128] Although not all aspects of
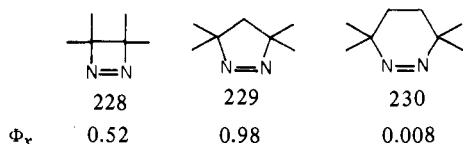
cyclic azoalkane photochemistry are understood, these data suggest that molecular flexibility is an important factor. Indeed, we shall see below that cis → trans isomerization becomes the major reaction for cyclic azoalkanes of more than six members.

It is noteworthy that Φ_r for diazetines **228** and **256** (Table XII) is less than unity, especially since no more than 1% of the missing quanta are accounted for by fluorescence.[128,336] Although the chemical yield of nitrogen is high in benzene, there appears to be a photoreaction between **228** and hexane. Electrocyclic ring opening of **228** to an azine has been considered[451] but not observed. Stereochemical studies of diazetine photolysis (e.g., on **336**) have yet to be reported. In view of the moderate Φ_r for photolysis of **228** and **256**, the reported inertness[452] of **547** is rather surprising. The latter diazetine was
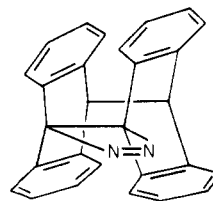

547

irradiated at 254 nm in benzene such that the solvent was the principal light absorber. Nevertheless, one would expect efficient triplet-energy transfer[453] from benzene to **547**. More worrisome than its photoinertness is the apparent absence of an azo band (~330 nm) for **547**. If the structure of **547** is correct, its triplet state must be nondissociative. A reinvestigation of this interesting compound is warranted in any case.

Whereas radiationless decay seems to be important in diazetines, the sum of Φ_r and Φ_f (fluorescence quantum yield) is unity for pyrazoline **229**. As seen in Table XII, the vast majority of pyrazolines decompose nicely under irradiation; in fact, this reaction is useful for the synthesis of cyclopropanes.[8,171–178] The only photostable pyrazoline prepared to date is **291**, whose Φ_r is 0.012[225] and Φ_f is 0.001.[336] The
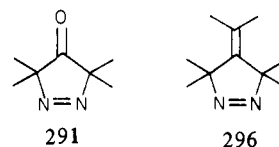
striking contrast between **291** and **296** is due to the far higher rate of radiationless decay in the former (10^8 vs. 10^6 s^{-1}).[454] As suggested by the PES spectrum,[255] mixing of carbonyl and azo orbitals in **291** could enhance the rate of ISC to an unreactive triplet state.

Direct photolysis of pyrazolines must occur from the singlet state; otherwise one would hardly expect to observe SCE's in so many cases (cf. IV.B.). In support of this view, Andrews and Day[340] showed that fluorescence of **297** was quenched by piperylene with the same Stern–Volmer slope as for decomposition. The observation that Φ_r for **296** changes from 0.31 to 0.86 on raising the temperature from 5 to 51.5 °C suggests that the excited singlet state encounters a barrier of 10 kcal mol^{-1} to loss of nitrogen.[455] Fluorescence of **296**, on the other
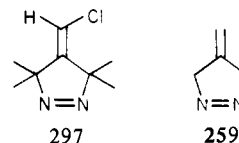
hand, decreases at elevated temperatures, corresponding to E_a = 7.9 kcal mol^{-1} for a competing process (decomposition).[455,456] The reasonable agreement between these figures deduced from totally independent measurements again supports photodissociation from the lowest singlet state. However, the sum of Φ_r and Φ_f is much below unity at 5 °C, suggesting that radiationless decay can become important. It is interesting to note in this regard that trimethylenemethane was first observed by low-temperature photolysis of **259**.[220,223] The feeble ESR signal

obtained by using this precursor in contrast to that from 3-methylenecyclobutanone can be rationalized if the sharp decline in Φ_r with temperature carries over to 259.

Photolysis of 256 and 472 should lead to isomeric diradicals D_N and D_Q, which are important in the norbornadiene–quadricyclene (N–Q) interconversion.[457] Whereas the triplet state of

256

472

N   Q
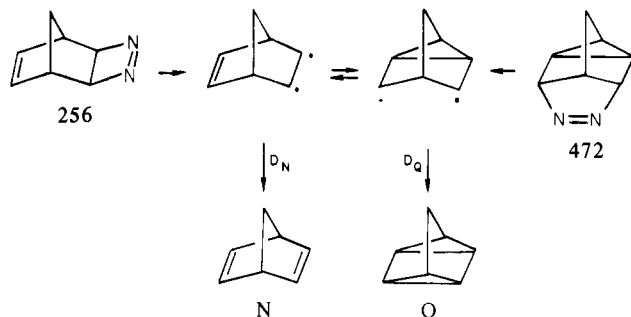
either azoalkane gave a 9:1 ratio of Q to N,[354] direct irradiation of 472 formed these products in a 0.6:1 ratio. It follows that intersystem crossing in 472, as in other pyrazolines at ambient temperature, is of minor importance. Cooling the irradiated solution to −78 °C, however, diminishes singlet decomposition and enhances ISC, thereby leading to more Q. Irradiation of 256 gave a N:Q ratio similar to that observed from the triplet state, implying that ISC is efficient for this fused diazetine. Since Φ_r for triplet-sensitized decomposition was essentially the same as for direct photolysis, it is likely that both reaction modes proceed via the triplet state of 256. The difference in ISC efficiency between 256 and 472 may be due to their different orbital ordering.[339,458] The results from these compounds suggest that the excited singlet surface connecting N and Q possesses a minimum which delivers singlet diradicals mostly to N and that the minimum in the excited triplet surface is located such as to deliver triplet diradicals preferentially to Q. This conclusion is in good agreement with theory[234,459] and with the photochemical behavior of hydrocarbons N and Q.

In another clever application of azoalkane photolysis to a diradical problem, Zimmerman et al.[460] carried out thermolysis and direct and sensitized photolyses of 524, 525 (Table XII), and 548. Thermolysis gave only barrelene (549) or its benzo

548   549   550

551   552
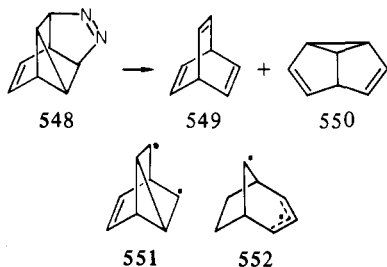
analogues, but triplet sensitization led almost exclusively to semibullvalene products (550). Since the triplet diradicals produced from the pyrazolines exhibited the same photochemistry as sensitized irradiation of the three barrelenes, it is likely that these diradicals lie on the barrelene di-π-methane rearrangement pathway. The corresponding singlet diradicals, on the other hand, undergo only the Grob fragmentation (551 → 549). Direct irradiation of the azoalkanes gave products of both the 549 and 550 type, suggesting that S_1 leads to barrelenes and that ISC is incomplete. As in the D_N–D_Q case discussed above, the product distribution is consistent with a tight geometry for singlet diradicals (551 → 549) and a loose geometry for triplet diradicals (552 → 550).[459]

Irradiation of pyrazolines can sometimes lead to diazo compounds by retro-1,3-dipolar cycloaddition (cf. II.C.3.b). This reaction is known for such 3H-pyrazoles as 553 and it is likely in many others.[462-484] Cyclopropyl fused systems (e.g., 293

553
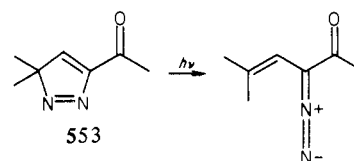
in section II.C.3.b, 522, 554, 555) also rearrange to photolabile

522   554   555
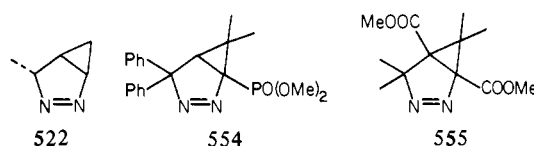
diazo compounds; in fact, even 3,5-diphenyl-1-pyrazoline (303) undergoes this reaction.[465] Photolysis of 303 at 77 K had

303
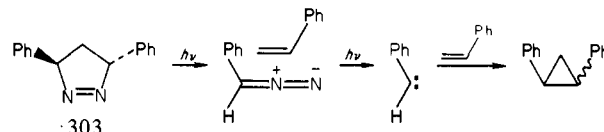
earlier[192] been shown to give an ESR signal, but more recent work[465] at 5.5 K revealed the spectrum of phenylcarbene. This intermediate, which arises by photolysis of phenyldiazomethane, can react with styrene as shown above to give the same product as expected directly from 303. On account of this complication, it could only be stated that at least 10% of 303 undergoes retro-1,3-dipolar cycloaddition. The same mechanism could occur in 3,5-divinyl-1-pyrazoline (273, 274),[195] though it does not occur in 556, which prefers instead the unusual electrocyclic elimination illustrated below.[466]

556
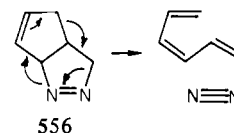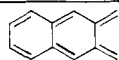
The fates of diazetine and pyrazoline singlet states are mostly decomposition plus some intersystem crossing and fluorescence. In contrast, six-membered azoalkanes (e.g., 230) exhibit no fluorescence and only very inefficient decomposition.[128] Obviously Φ_r is not exactly zero under direct or sensitized irradiation; otherwise, the SCE study of 323[251] would not have been possible. Whereas extensive tautomerization was observed[142] on irradiation of 3,6-diphenyltetrahydropyridazine (324), the absence of α hydrogens precludes this reaction in 230. Photoisomerization to the cyclic trans-azoalkane followed by thermal reversion to the cis isomer was suggested[128] as the energy-wasting process in 230, but the trans isomer was not detectable by matrix isolation IR.[467] Since this reaction is known in a seven-membered azoalkane,[268] excited 230 probably loses its energy by twisting without actually forming the trans isomer. Φ_r for six-membered azoalkanes can be increased 25-fold by making them more labile thermally, e.g., 319 and 523;[455] how-

319   523
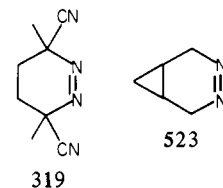
ever, radiationless decay still accounts for 80% of the absorbed photons in these moderately flexible rings.

The photochemistry of cyclic azoalkanes larger than six members resembles that of their acyclic counterparts in that both isomerization and decomposition can occur. Direct or sensitized irradiation of 557 converted it to the trans isomer 558

TABLE XIV. Unstable Species Generated from Azoalkane Photolysis

species	method of observation	ref
	UV-vis	267, 268
	UV-vis, ESR	268, 468, 469
	ESR, UV-vis	416, 479
	UV-vis	479
	ESR	472
	ESR	a
	UV-vis, fluorescence	267
	ESR, UV-vis, fluorescence	303, 469
	ESR	220, 223
	ESR	319
	ESR	265
	NMR	195

^a Closs, G. L.; Kaplan, L. R.; Bendall, V. I. *J. Am. Chem. Soc.* 1967, *89*, 3376.

which is stable enough to be isolated[268] but tautomerizes in ethanol.[468] The fact that **558** reverts thermally to **557** (half-life
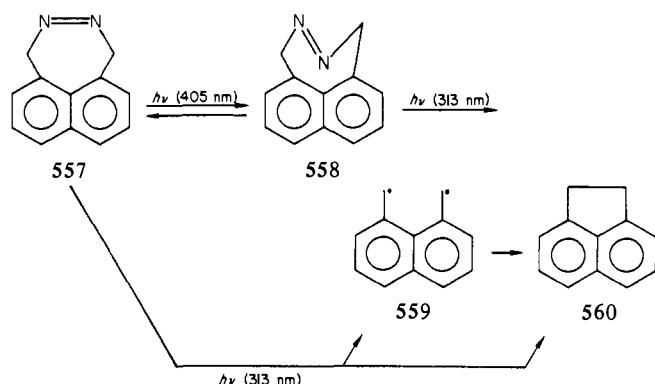
= 40 min at 25 °C) stands in remarkable contrast to the behavior of acyclic *cis*-azoalkanes such as ATB. Referring to Figure 7, one would expect the strain of **558** to raise its trans ground-state energy above that of the cis isomer (*trans*-cycloheptene has a strain energy of 27 kcal mol^{-1}[444]); moreover, benzylic stabilization of **559** should lower the decomposition transition state below that shown in Figure 7. Since these changes still predict that **558** should decompose rather than isomerize, the geometry of this isomer must allow negligible resonance stabilization of the transition state for decomposition. That cis → trans isomerization can be effected by benzophenone is analogous to the results in the acyclic series (see

IV.A.2) and in eight-membered rings. Since **558** is surely more strained than **557**, triplet sensitization converts the cis isomer to the trans regardless of which isomer is of higher energy content. The quantum yield for **557** → **558** under direct irradiation is one-tenth that of the reverse process, whereas these Φ's are equal in acyclic azoalkanes. Apparently the ring strain of **558** influences the manner in which the excited state partitions between the two ground-state isomers. Irr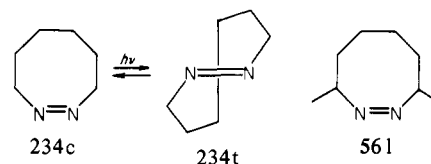adiation of either isomer at a shorter wavelength (313 nm) bypasses isomerization in favor of decomposition to acenaphthene (**560**) and diradical **559**, which closes to acenaphthene on warming.[468,469] The triplet state of **559** is one of a considerable number of diradicals which have been generated from azoalkane photolysis and observed spectroscopically (cf. Table XIV).

Irradiation of the parent eight-membered azoalkane (**234c**) converted 60% of it to the cyclic trans isomer (**234t**), which could be isolated by column chromatography and photoisomerized back to the cis compound.[470] Note that this intercon-

version is calculated to be thermoneutral (cf. Table VII). Extended irradiation of **234c** (15% completion in 72 h) gave 1-hexene (70%) and cyclohexane (30%).[415] Whereas **234c** was said to be unaffected by irradiation in the presence of benzophenone for 168 h, Quinkert et al.[365] showed that, as in the case of AIP,[90] this sensitizer led to a 15:85 mixture of **234c** and **234t** without loss of nitrogen. The report[415] that **561** exhibited a SCE on irradiation with fluorene as sensitizer is unexpected in view of the ability of fluorene to transfer singlet energy.[394]

The original work[271] on the diphenyl analogues of **234** contained an incorrect structural assignment which created some confusion about the results in this series. The standard method of converting azines to azoalkanes gave two compounds whose properties are shown above. Although these products were assigned structures A and B, their widely different thermal stabilities led Neuman and Ertley[112] to suggest that A possessed a trans azo linkage. The eventual synthesis of all four isomers

	A	B
μ, D	1.20	2.86
λ_{max}, nm (ϵ)	368 (45)	381 (111)
mp, °C	90	115
E_a, kcal mol^{-1}	36.7	26
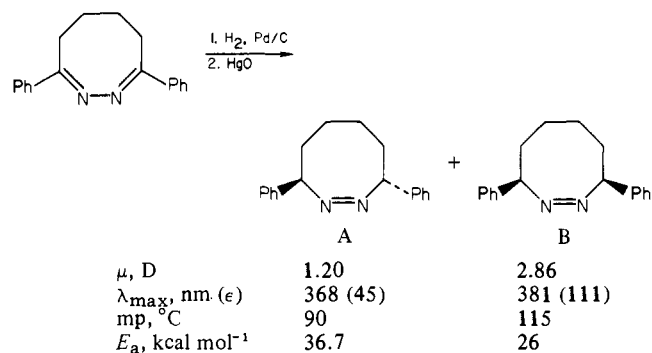
(**327, 328, 562, 563**)[365] confirmed this suspicion and showed that the lower melting compound made by Overberger et al.[271] was in fact **327**. (Isomer B was correctly assigned as **562**.) The report[271] that **562** tautomerized 1000 times faster than **327** is in accord with the greater reactivity of *cis*- than *trans*-azoalkanes. However, since the relative energy of the four isomers is unknown (cf. Table VII), the usual explanation based on thermodynamic stability does not necessarily apply here. Direct irradiation of **327** gave 65% 1,6-diphenyl-1-hexene and 35% 1,2-diphenylcyclohexane.[415] Benzophenone sensitization proceeded readily, as in acyclic azoalkanes bearing a radical-stabilizing group, and produced over 95% of the olefin. Although this change in product ratios was interpreted as another

327 → 328

562 →s*3→ 563
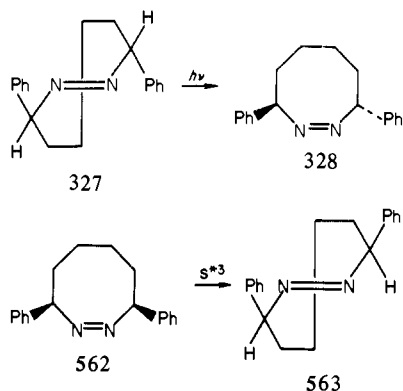
SCE, it was later discovered[365] that direct irradiation of **327** first produces **328**, which decomposes thermally at ambient temperatures. As in the case of **234**, direct or sensitized irradiation of **562** gives the cyclic trans isomer **563**.

D. Bridged Bicyclic and Polycyclic Azoalkanes

Detailed studies of the simple bicyclic azoalkanes DBH, DBO, and **231** were carried out some years ago.[343,355,471] Whereas

DBH   DBO   231
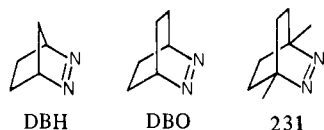
DBH decomposes in solution with a unit quantum yield, singlet DBO and **231** decay radiationlessly or fluoresce, depending on the solvent.[336] In the gas phase, higher pressures quench the weak fluorescence of DBH without substantially changing Φ_r. These results were taken to mean that DBH is subject to collision-induced dissociation.[343] Irradiation of DBH in a matrix at 5.5 K produces cyclopentane-1,3-diyl radicals (**564**), which were observed by ESR to have a triplet ground state.[472] However,

DBH →s*3→ 564 →O₂→ 565
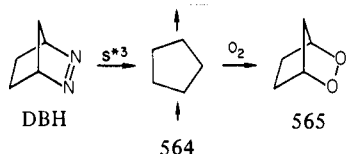
simple derivatives of DBH, which are accessible by a new synthetic method,[473] gave markedly weaker diradical ESR spectra or no spectra at all.[472] In a remarkable reaction, benzophenone-sensitized photolysis of DBH under 150 psi of oxygen leads to peroxide **565**.[474] If this transformation represents trapping of **564**, its lifetime, which is governed by the rate of spin inversion, must be relatively long. This rate depends mainly on a low preexponential factor ($A \sim 10^8$) since the barrier to spin inversion and ring closure of **564** is only 2.3 kcal mol⁻¹.[472,475]

A brief synthesis of triquinacene (**567**) was based on photolysis of the polycyclic azoalkane **566**.[476]

566 →hv→ 567
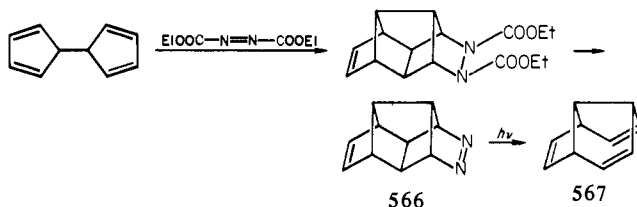
Direct or sensitized irradiation of **471** induces loss of nitrogen with $\Phi_r = 0.54$ and 0.3, respectively.[327,336] The percentage of diazocene **568**, the major product of triplet-sensitized irradiation, was found to increase as oxygen was added to the directly irradiated solution. These results suggest that oxygen enhances

471 →hv→

568

the intersystem crossing of **471**. It was further discovered that whereas **568** is formed in >70% yield at -78 °C,[326] it accounts for only 8% of the product at 25 °C. Decomposition of excited singlet **471** was postulated to encounter a thermal barrier, such that ISC becomes more important at low temperatures.[327]

448 decomposes photochemically at 25 °C with $\Phi_r = 0.95 \pm 0.05$ and a fluorescence yield of about 0.1%.[297] Loss of
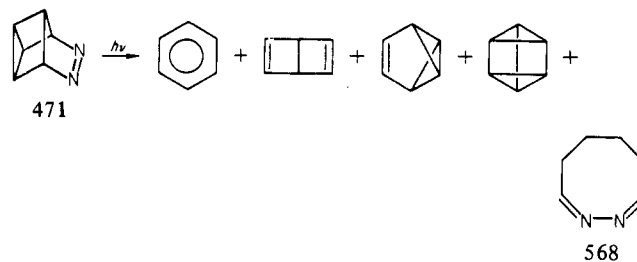

569 ←hv/-78 °C← 448 →hv/-196 °C→ 449
-40 °C
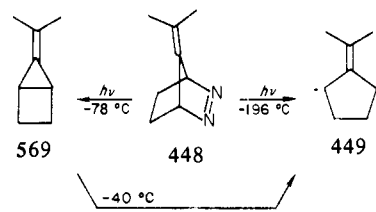
nitrogen occurs directly from the singlet state, though triplet sensitization can be effected with xanthone. In the latter case, the products exhibit the low fused/bridged adduct ratio characteristic of the triplet diradical (cf. II.D).[227] Irradiation of **448** at -196 °C gives a well-defined ESR spectrum of **449**, whose triplet ground state[477] lies between 0.6 and 3.5 kcal mol⁻¹ below the singlet.[290,416] Although theoretical calculations predict a splitting of about 20 kcal mol⁻¹ for trimethylenemethane itself, this value may not apply to **449**.[475] Irradiation of **448** at -78 °C was recently found to produce the ring-closed product **569** in virtually quantitative yield.[478] On being warmed to -40 °C, this compound opened to diradical **449** with activation parameters $E_a = 16.9$ kcal mol⁻¹ and $\Delta S^{\ddagger} = -16$ eu. The extraordinarily low ΔS may signify a spin-forbidden transition state. These observations may be rationalized if irradiation of **448** initially gives singlet **449** at all temperatures. The expected low E_a and low $\Delta S^{\ddagger}$ for ISC relative to the higher E_a and $\Delta S^{\ddagger}$ for ring closure would favor ISC from singlet **449** to triplet **449** at -196 °C. Ring closure to **569** dominates at -78 °C, but this intermediate has a half-life of only 2 s at 25 °C. Although **569** is not the first capturable intermediate in the photolysis of **448**,[297] it should coexist with triplet **449** at 25 °C in dilute solution where dimerization is unfavorable. Optical and fluorescence spectra have been obtained on both **449** and its diphenyl analogue at -196 °C.[479]

The photochemistry of azoalkanes containing the bicyclo-[2.2.2] moiety is more complex than that of the [2.2.1] compounds. Steel and co-workers[343,471] have studied DBO rather extensively, and their results are summarized in Scheme XI. The hydrocarbon products are those of ring closure and ring opening, signifying the intermediacy of a diradical. Photolysis in solution produces a quencher which inhibits decomposition and fluorescence;[471] moreover, the yield of nitrogen is only about 50%. Although the quencher has not been isolated, it probably arises from photoreduction of the azo group, as in the case of **570**.[480] In fact, hydrogen abstraction by azo esters and aryl

570
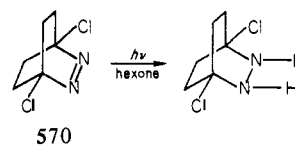
azo compounds is well-known,[481] and intramolecular cyclo-

SCHEME XI. Decomposition of DBO

gas phase

solution
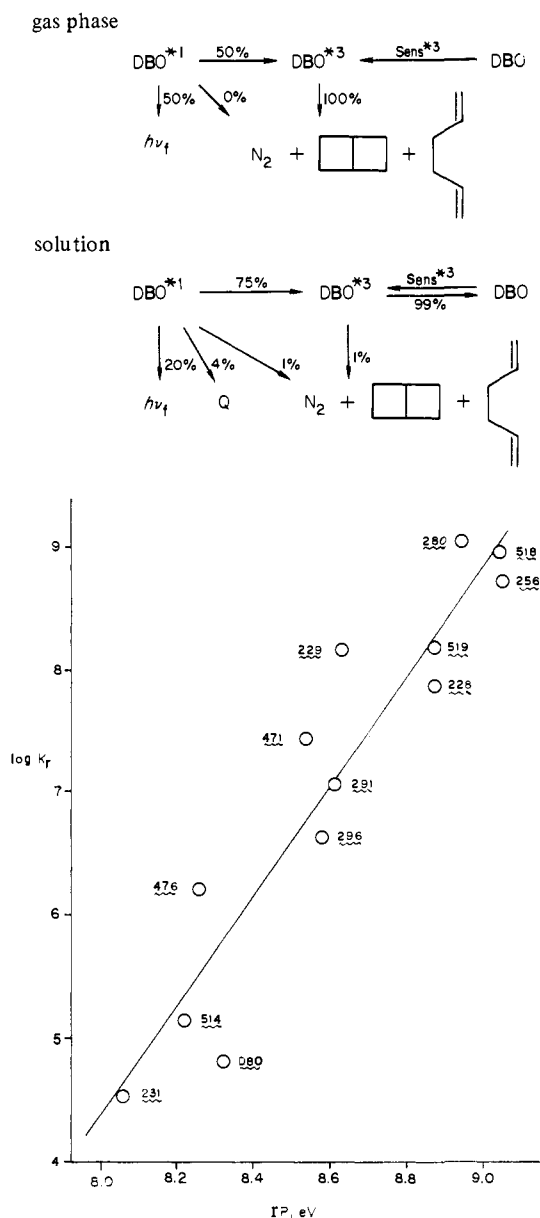
Figure 13. Log of the rate constant (k_r) for decomposition of singlet excited cyclic azoalkanes vs. their lowest ionization potential. Compound numbers are shown next to each point.

addition of a bicyclo[2.2.2]azoalkane was reported recently (**571** → **572**).[482]

The triplet state of DBO and **231** has a very effective pathway for radiationless decay, as demonstrated by the low Φ_r and lack of phosphorescence in these compounds, even when their triplet is produced by sensitization in a frozen glass.[355] Thus the large difference in singlet reactivity between DBH and DBO carries over to the triplet state. Since both states are of higher energy in DBH,[355,471] any barrier to decomposition should be more easily sur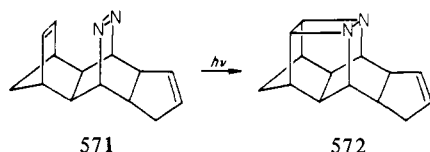mounted in this case. It is fascinating to note that a reactivity difference similar to that between DBO and DBH is found in the photochemistry of norbornene and bicyclo[2.2.2]octene.[483]

Several attempts have been made to correlate azoalkane photoreactivity with the lowest ionization potential of these

molecules. Houk, Chang, and Engel[334] noticed that compounds whose IP was higher than expected on the basis of inductive effects lose N_2 readily (DBH and **229**) whereas those with normal IP's (**231** and **230**) exhibit low Φ_r's. This correlation was made more quantitative by plotting log k_r, determined from lifetime and Φ_r measurements, vs. IP(n_).[336] (cf. Figure 13). The observed trend was rationalized as follows.[336] For cis-diimide, both the NH bond strength and IP are dependent on the NNH angle. As the IP increases, signifying a lower energy for the n_ orbital, the NH bond becomes weaker. Removal of an electron from the n_ MO of azoalkanes by excitation apparently weakens the C–N bond and enhances k_r to an extent dependent upon IP. It will be interesting to see whether this correlation holds for 1-vinyl-DBO (**466**; see below).

Other azoalkanes containing the bicyclo[2.2.2] moiety have also proven resistant to photolysis (**508**,[328] **510**,[330] **515**[332]). At
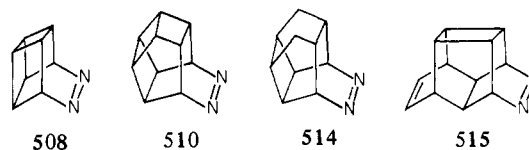
least half of the absorbed photons were emitted as fluorescence in the case of **510** and **514**. Although Φ_r for **514** was only 0.01 in hexane,[336] gas-phase photolysis gave the products shown below.[331] Unless their Φ_r is already unity, all azoalkanes lose
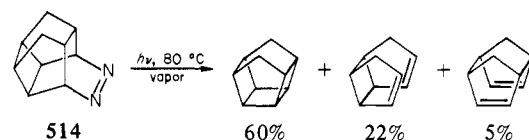
nitrogen more efficiently at higher temperatures.[327,373,375,381,390,455] Turro and co-workers[456] used the temperature dependence of fluorescence intensity to calculate the activation energy (E_a) for decomposition of the excited singlet state. When E_a is greater than about 6 kcal mol⁻¹, this technique fails and the temperature dependence of Φ_r must be determined. In the case of **231**, E_a was found to be 7.3 kcal mol⁻¹.[455] The sharp decline of Φ_r with temperature explains why lengthy irradiation of DBO at 5.5 K produced no ESR signal.[472]

It was discovered recently[455] that as in monocyclic six-membered azoalkanes, Φ_r for bicyclo[2.2.2] compounds can be enhanced greatly by certain structural changes which render these compounds more labile thermally. As seen from the results for **458**, **475**, and **466** (Table XII), incorporation of radical-stabilizing substituents or an exocyclic cyclopropyl ring raises Φ_r to nearly unity. Even an exocyclic cyclobutyl ring (**476**) increases Φ_r, but an endocyclic cyclopropyl ring (**477**) causes no further enhancement. Other [2.2.2] systems containing endocyclic cyclopropyl rings are known to decompose photochemically (**481**[316] and **573**[417]), but no quantum yields were reported. Moreover, deazatization of these two compounds
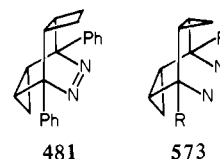
is already facilitated by bridgehead radical-stabilizing groups.

In seeking an explanation for the effect of structure on Φ_r, it was noted that τ_f was 420 ns for DBO but was less than 0.5 ns for **466**.[455] This result is inconsistent with decomposition from a state which precedes A_0^1[344] since the vinyl group should accelerate loss of N_2 from such a state without affecting τ_f. The earlier hypothesis[344] was based on the fact that changing solvent from MeOD to MeOH decreases Φ_f and τ_f of **231** about tenfold,

yet the quantum yield for loss of azoalkane is hardly affected. These results, however, are equally well accommodated if $A_0{}^1$ forms a hydrogen-bonded complex considerably faster with MeOH than MeOD. Assuming that one-fourth of either complex undergoes reaction, one can predict from the experimental Φ_f's the correct Φ for disappearance of azoalkane. It should be recalled that Φ_r is much below Φ_{-azo} in this system, so chemical reaction with MeOH is very plausible.

The substantial decrease in τ_f and increase in Φ_r on incorporation of a bridgehead vinyl group (DBO vs. **466**) allow one to calculate that k_r is increased over 10 000-fold by this structural change. Since the $A_0{}^1$ state of DBO experiences a barrier to decomposition, the barrier height must be greatly reduced when the bicyclic azoalkane is made more labile thermally. Thus the excited-state barriers seem to mimic the behavior of the ground state. In terms of theory,[110] the crossing point of the $^1(n,\pi^*)$ surface with the dissociating $^3(\pi,\pi^*)$ curve should be lowered when the incipient radicals are stabilized (cf. Figure 12).

Certain azo compounds containing the bicyclo[2.2.2] skeleton exhibit medium-dependent photochemical behavior.[484] For example, **574** gives **575** on irradiation in solution, but the pre-

sumed diradical intermediate closes to **576** in frozen benzene. **479** behaves similarly. In contrast, the saturated analogue of **574** is photochemically inert in frozen benzene for reasons which are as yet unclear.
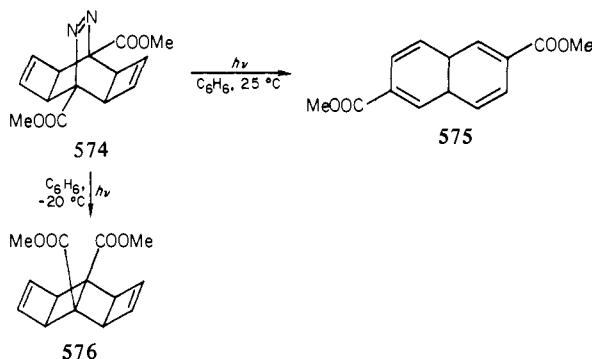
V. Conclusion

It is apparent from the foregoing discussion that much is known about the decomposition of azoalkanes. Their thermal stability is governed by ground-state energy, stability of the incipient radicals, and orbital symmetry factors. Acyclic cis-azoalkanes, which are produced by irradiation of the trans isomers, are of higher energy and lose nitrogen more readily than trans-azoalkanes. Decomposition generally takes place by simultaneous breaking of both C–N bonds, whereas thermal isomerization, when it occurs, probably follows the semilinearization pathway. Special reactions are observed in the lower cyclic azoalkanes; for example, diazirines and some pyrazolines isomerize to diazo compounds whereas other pyrazolines decompose ionically. In the six-membered rings, there exists a rough correlation between photochemical and thermal reactivity. Nearly two dozen interesting hydrocarbons and diradicals have been generated by thermolysis and photolysis of cyclic and bicyclic azoalkanes. Triplet-sensitized decomposition of thermally labile acyclic azoalkanes can lead to a spin correlation effect, many examples of which are known in the cyclic series.

Notwithstanding these advances in azoalkane chemistry, several difficult problems remain. In the thermolysis area, the stereochemistry of alkylpyrazoline thermolysis and the failure of azoalkane decomposition rates to correlate with bridgehead radical stability are still not fully explained. More pressing questions remain open in azoalkane photochemistry, especially concerning the elusive triplet state. When does intersystem crossing occur and why is the triplet state so short-lived? By presenting the results obtained to date, the author hopes to stimulate research which will ultimately answer these questions.

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