

Linnett Structures for Homolysis Transition States. The Bridgehead Azo Anomaly¹

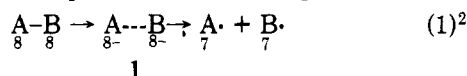
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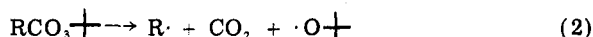
The transition states of two radical-forming reactions, pyrolyses of *tert*-butyl peresters and azo compounds, are shown as Linnett structures. The perester reaction is seen to be a least-motion process, but not the azo decomposition. In the latter, the first developing radical center, tetrahedral in the ground state, must pass through a planar intermediate state before becoming a free radical. Planarity is necessary to minimize L-strain in that particular electronic configuration which is transiently experienced on the azo but not on the perester reaction coordinate. Data are adduced to support the Linnett transition states for both reactions with regard to shape, degree of bond breaking, and charge distribution. In this way some hitherto unexplained anomalies in the behavior of azo compounds, such as the abnormally great stability of bridgehead and some highly strained cage derivatives, can be understood.

Homolysis of a single bond is an apparently simple process, in which the bond simply stretches until it breaks, as in eq 1. Such a process would be expected to be a

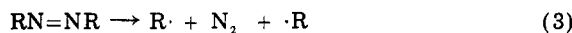


least-motion one, in which geometric and electronic changes in the substructures of A and B occurred smoothly during progress along the reaction coordinate (RC)³ from A-B to A· + B· and in which the Bell-Evans-Polanyi-Hammond⁴ (BEPH) principle applied; i.e., any factor that affected the stability of the product radicals would also be reflected in the energy of the transition state (TS)³ 1 and in the energy of activation (*E_a*),³ because the product radicals' properties have already come partially into existence at the TS. In fact, a process as simple as this could be imagined for any chemical reaction, and it is particularly those cases in which either the least-motion or BEPH principle is contravened that arouse interest and require explanation.

An important class of reactions to which the BEPH principle does not apply is the formation of radicals by homolysis of azo compounds. Thus, although the *tert*-butyl and 1-adamantyl radicals are formed with equal facility in the pyrolysis of *tert*-butyl peresters (eq 2), an extra impediment of 19 kcal/mol to the formation of the 1-adamantyl radical relative to *tert*-butyl exists with the azo compounds (eq 3). The peculiarity resides in the azo



R	<i>t</i> -Bu	1-Ad
relative rate ⁵	1	1.4
ΔH^\ddagger	30.0	29.8



R	<i>t</i> -Bu	1-Ad
relative rate ⁶	1	0.0004
ΔH^\ddagger	43.9	63.0

(1) Application of the Linnett Electronic Theory to Organic Chemistry, Part 7. Part 6: R. A. Firestone, *J. Chem. Soc., Chem. Commun.*, 163 (1973).

(2) Numbers (7 or 8) under or next to atoms refer to the number of electrons in the outer shell.


(3) Glossary: RC, reaction coordinate; BEPH, Bell-Evans-Polanyi-Hammond; TS, transition state; *E_a*, energy of activation; MPRC, midpoint of the reaction coordinate; ERG, electron-releasing group; EWG, electron-withdrawing group; GS, ground state.

(4) R. P. Bell, *Proc. R. Soc. London, Ser. A*, 154, 414 (1936); M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 32, 1340 (1936); G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

(5) L. B. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, 46, 3099 (1968).

Table I. Stability of Bridgehead Radicals^a

$\text{RCO}_2-\text{O}-\text{C}(\text{O})-\text{R} \rightarrow \text{R} \cdot + \text{CO}_2 + \cdot \text{O}-\text{C}(\text{O})-\text{R}$	(a) ⁵
$\text{R}-\dot{\text{C}}\text{O} \rightarrow \text{R} \cdot + \text{CO}$	(b) ⁷
$\text{R}-\text{I} + \text{Ph} \cdot \rightarrow \text{R} \cdot + \text{PhI}$	(c) ⁸
$\text{R}-\text{Br} + \text{Bu}_3\text{Sn} \cdot \rightarrow \text{R} \cdot + \text{Bu}_3\text{SnBr}$	(d) ⁹

reaction	relative rates for R =				
	<i>t</i> -Bu	1-Ad	(222)	(221)	
a	1	1.4	0.10	0.00022	
b	1	2.5	1.2	0.0068	
c	1	0.61	0.51	0.16	
d	1		0.42	0.32	0.019

^a For a review see ref 10.

compounds and not the peresters, because by a variety of kinetic criteria (Table I), the stability of the 1-adamantyl radical is normal for a tertiary unstrained radical. Carbon radicals tend to be planar or nearly so,¹¹ and apparently the adamantyl bridgehead can accommodate these requirements without strain. A greater resistance to bridgehead planarity exists for the 1-bicyclo[2.2.2]octyl radical, which forms a little more sluggishly than 1-adamantyl, and there is still more resistance with 1-bicy-

(6) M. Prochazka, O. Ryba, and D. Lim, *Collect. Czech. Chem. Commun.*, 33, 3387 (1968).

(7) D. E. Applequist and L. Kaplan, *J. Am. Chem. Soc.*, 87, 2194 (1965).

(8) T. J. Tipton and D. G. Saunders, *J. Am. Chem. Soc.*, 93, 5186 (1971).

(9) R. C. Fort, Jr., and J. Hiti, *J. Org. Chem.*, 42, 3968 (1977).

(10) R. C. Fort, Jr., and P. R. Schleyer, *Adv. Alicycl. Chem.*, 1, 284 (1966).

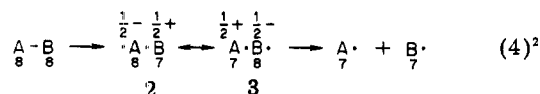
(11) CH₃ planar or easily deformed pyramidal: G. Herzberg, *Proc. R. Soc. London, Ser. A*, 262, 291 (1961); L. Kaplan, "Free Radicals", Vol. 2, J. K. Kochi, Ed., Wiley, 1973, p 363ff.; J. M. Hay, "Reactive Free Radicals", Academic Press, 1974, p 44; J. Dyke, N. Jonathan, E. Lee, and A. Morris, *J. Chem. Soc., Faraday Trans. 2*, 1385 (1976); L. Bonazzola, N. Leray, and J. Roncin, *J. Am. Chem. Soc.*, 99, 8348 (1977); G. B. Ellison, P. C. Engelking, and W. C. Lineberger, *ibid.*, 100, 2556 (1978). CR₂ nonplanar: D. E. Wood, L. F. Williams, R. F. Sprecher and L. A. Lathan, *ibid.*, 94, 6241 (1972) (but see M. C. R. Symons, *Tetrahedron Lett.*, 207, 1973); P. J. Krusic and P. Meakin, *J. Am. Chem. Soc.*, 98, 228 (1976); D. Griller, K. U. Ingold, P. J. Krusic, and H. Fischer, *ibid.*, 100, 6750 (1978); T. Koenig, T. Balle, and J. C. Chang, *Spectrosc. Lett.*, 9, 755 (1976). Bridgehead radicals somewhat flattened but still pyramidal: P. J. Krusic, T. A. Rettie, and P. R. Schleyer, *J. Am. Chem. Soc.*, 94, 995 (1972). Bicyclic radicals pyramidal: T. Kawamura, T. Koyama, and T. Yonezawa, *ibid.*, 95, 3220 (1973); Y. Sugiyama, T. Kawamura, and T. Yonezawa, *J. Chem. Soc., Chem. Commun.*, 804 (1978).

clo[2.2.1]heptyl, which forms much more slowly.

Another way of highlighting the bridgehead azo problem is through Polanyi plots of E_a for decomposition vs. radical stability, as measured by the bond-dissociation energies of the radical-H bonds. Both *tert*-butyl peresters and azo compounds give linear Polanyi plots that include many examples, indicating obedience to the BEPH principle.¹² However, if the 1-adamantyl cases are added to both plots, assuming the bond energy of 1-Ad-H to be equal to that of *t*-Bu-H, the perester falls right in with the normal group, but the azo does not, lying far above the regression line.

Apparently, then, azoadamantane is endowed with an extra measure of thermal stability which it owes to a TS effect and not to product development control; i.e., the BEPH principle fails in this instance. The thesis now offered is that this failure arises from azo compounds decomposing via a *non-least-motion* pathway, in contrast to most other radical-forming reactions such as perester thermolysis. This idea is not new, having been proposed on other grounds (and in other, but equivalent, terms) by Ruchardt¹³ and Roth¹⁴ and their co-workers. The novelty here lies in providing a detailed description of the overall process by means of Linnett structures.^{15,16}

Unlike eq 1, the Linnett description of single-bond homolysis (eq 4) is more complex, involving two different

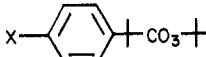


resonance forms¹⁷ for the intermediate state that exists at the midpoint of the reaction coordinate (MPRC),³ $2 \leftrightarrow 3$. It is important to realize that the MPRC may or may not coincide with the TS; for an endothermic cleavage to radicals, one expects a late TS, standing between the MPRC and the product radicals.

The basic principles to be used in eq 4 are the following: (1) the bond breaks one electron at a time, so that at the MPRC a one-electron bond exists; (2) the temporary charge transfer created by (1) is influenced in direction by the electronegativity of the attached groups; (3) bonding is maximized at the TS everywhere, except at the breaking bond, by bringing into bonding orbitals single nonbonded electrons on atoms adjacent to atoms whose valence shells contain less than eight electrons;^{15,16,18} (4) bond angles in the Linnett structures may differ from those in reactants and products; and (5) primary and secondary L-strain¹⁷⁻¹⁹ is minimized. If A and B are not the same, then one or the other resonance form of the MPRC will dominate the resonance hybrid, with consequences on both its geometry and charge distribution that can be predicted from the Linnett structures.

L-Strain may be described as follows. Covalent bonds are strongest when the bonding electrons' orbitals lie on the internuclear line. L-Strain, which can exist in both ground and transition states, arises when forces elsewhere in the molecule compel the bonding electrons to move off the internuclear line in opposite directions, in order to

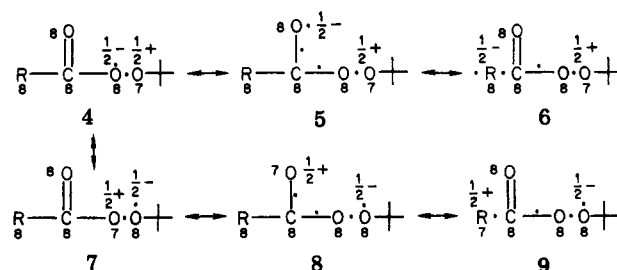
Table II. Substituent Effects on Perester Decompositions


 $\rho = -0.75 \text{ to } -1.20^{20}$

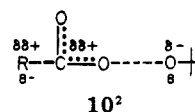
	R	relative rate
RCH ₂ CO ₂ +	H	1 ²¹
	Ph	363
	CH ₃ O	2 × 10 ⁶
	CN	0.0045
RCO ₂ +	CH ₃	1 ^{21b,21c,22}
	Et	2
	<i>i</i> -Pr	50
	<i>t</i> -Bu	300
	(<i>t</i> -Bu) ₂ CH	335
	Ph	1 ²³
	<i>p</i> -Tol	1.3
	mesityl	11
	2,4,6-(<i>t</i> -Bu) ₃ Ph	29

maintain the integrity of the spin sets. Bonds are weakened but not bent by L-strain. Illustrations are the C-R bonds in structures 17-19, and the N-R' bond in 20 (vide infra).

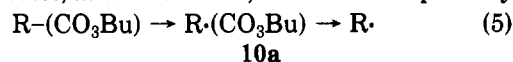
Consider first the MPRC canonical forms for perester thermolysis, 4-9.² Forms 4 and 7 correspond to moving



the electron out of the breaking bond to one side or the other as in 2 and 3. All six structures have the same number of bonding electrons, so on this score they are equivalent. Pairs 4 and 7, 5 and 8, and 6 and 9 are well balanced with regard to electron correlation and charge separation. However, there is one important difference between the two rows in that 9 is much lower in energy than 6 because it has lower L-strain and because the partial charges are allotted more favorably with regard to electronegativity, and in fact 9 is somewhat superior to all the others in this quality. Consequently the resonance hybrid can be expected to look like 10, in which O-O bond



breaking is advanced, R-C bond breaking is retarded, the departing *tert*-butoxy bears a fractional negative charge, and R has a smaller fractional positive charge. The succession of states undergone by R as the RC is traversed (eq 5) constitutes, as will be shown, a least-motion pathway



for R. That is why perester decomposition has no bridgehead anomaly.

Structure 10 fits the known attributes of perester pyrolyses well, as seen in Table II. The negative ρ and the

(12) P. S. Engel, A. I. Dalton, and L. Shen, *J. Org. Chem.*, **39**, 388 (1974).

(13) J. Hinz and C. Ruchardt, *Justus Liebigs Ann. Chem.*, **765**, 94 (1972).

(14) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.* **702**, 1 (1967).

(15) J. W. Linnett, *J. Am. Chem. Soc.*, **83**, 2643 (1961).

(16) J. W. Linnett, "The Electronic Structure of Molecules", Methuen, London, 1964.

(17) R. A. Firestone, *Tetrahedron Lett.*, 971 (1968).

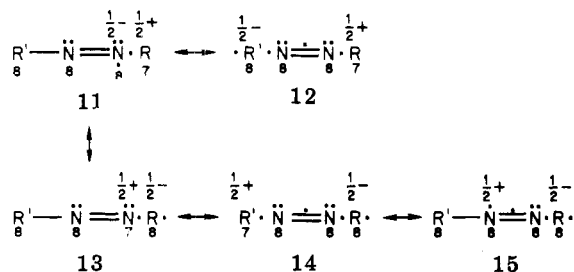
(18) R. A. Firestone, *J. Org. Chem.*, **34**, 2621 (1969).

(19) R. A. Firestone, *J. Org. Chem.*, **36**, 702 (1971).

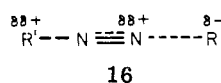
(20) P. D. Bartlett and C. Ruchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960); C. Ruchardt and H. Bock, *Chem. Ber.*, **100**, 654 (1967); J. P. Engstrom and J. C. Du Bose, *J. Org. Chem.*, **38**, 3817 (1973).

accelerating effect of conjugating and electron-releasing groups (ERG) jibe with development of positive charge on the incipient radical. Particularly noteworthy is the rate-retarding effect of α -cyano, a strongly electron-withdrawing group (EWG) whose influence can only be on the TS since it is a radical-stabilizing substituent. Cyano is thus anti-BEPH, although the question of least motion is not involved here. The modest accelerations brought about by groups that are bulky but not immense indicate little relief of ground-state (GS) strain in the TS, i.e., not much stretching of the R-C bond.

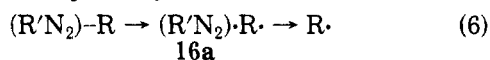
For azo decomposition the MPRC canonical forms are 11–15.² This ensemble differs from the earlier one (4–9)



in that one of the group, 15, is outstanding in stability because it has one more bonding electron than any other. This energy advantage—half a bond—is so large that other differences are minor by comparison. Therefore the resonance hybrid must resemble 16, in which breaking of one



N-C bond is much more advanced than the other, and the departing radical R bears a fractional negative charge, the opposite sign from that in the perester. The uniqueness of the azo MPRC lies in the fact that, in the two canonical forms 11 and 13 that correspond to the two basic forms 2 and 3, one of them, 13, has an atom with seven valence electrons next to a heteroatom. It is one of the features of Linnett's theory that such a system can gain additional stabilization energy by allowing the heteroatom to share one electron of its lone pair with the unsaturated atom, thus raising the multiplicity of the bond between them by one-half.^{15–18} The succession of states undergone by R as the RC is traversed is shown in eq 6, which (vide infra) is not a least-motion pathway for R.



It should be recognized that, although logically 16 seems poised to break the bond to R first and to R' afterward, the present mechanism does not require this, since 16 could conceivably go on to break both bonds simultaneously; thus either one- or two-bond scission is allowed, or perhaps sometimes one and sometimes the other. What is required is that bond breaking, whether concerted or not, be non-synchronous.

Table III shows that all the attributes of 16 are sup-

Table III. Substituent Effects on Azo Decomposition (R'-N=N-R)

R'	R	relative rate	E_a	A, s ⁻¹	ref
Pr	Pr	1	45.1		24
Pr	allyl	10 ⁷	35.0		24
allyl	allyl	6 × 10 ⁷	33.5		24
<i>t</i> -Bu	<i>t</i> -Bu		43.9	3.0 × 10 ¹⁷	25
<i>t</i> -Bu	CMe ₂ CN		34.9	4.0 × 10 ¹⁶	25
CMe ₂ CN	CMe ₂ CN	1*	33.4	6.9 × 10 ¹⁶	25
Ad	CMe ₂ CN		34.3	2.2 × 10 ¹⁵	25
Ad	Ad		63.0	7.4 × 10 ²⁰	25
ΔS^\ddagger					
CMe ₂ OMe	CMe ₂ CN	5.6*	32	8 ± 6	26
CMe ₂ OMe	CMe ₂ OMe	3.5 × 10 ⁻⁵ *	41	16.5 (Ph ₂ O)	26, 27

ported by the experimental facts. Asymmetry of bond breaking can be seen by comparing lines 1, 2, and 3, lines 4, 5, and 6, lines 6, 9, and 10, and lines 6, 7, and 8. Thus in changing from (Pr, Pr) to (Pr, allyl), the radical-delocalizing allyl raises the rate and lowers E_a greatly, but changing further to (allyl, allyl) does comparatively little more. Similarly, in going from (*t*-Bu, *t*-Bu) to (2-CN-2-Pr, *t*-Bu), the EWG cyano lowers the E_a very much because it stabilizes the transient negative charge, while a second cyano as in (2-CN-2-Pr, 2-CN-2-Pr) has little further effect. With (2-MeO-2-Pr, 2-CN-2-Pr) the rate is about the same as with (2-CN-2-Pr, 2-CN-2-Pr), since only one side needs help from the cyano, but with (2-MeO-2-Pr, 2-MeO-2-Pr) the rate goes down and the E_a goes up markedly—almost in fact back to those for azoisobutane—because now the transient negative charge has no good electron sink. It is noteworthy that the effects of cyano and methoxy are the reverse of the perester situation, where it is positive rather than negative charge that wants delocalization. Finally, going from (2-CN-2-Pr, 2-CN-2-Pr) to (1-Ad, 2-CN-2-Pr) makes little change because there is still one good side, but with two adamantyls there is tremendous retardation, as seen earlier. In a survey of these and many other azo examples, it was concluded by Engel and Bishop that asymmetry of bond breaking, more or less, is the general rule.³²

Table IV deals further with the question of charge stabilization, emphasizing once more that conjugating groups and EWG's facilitate the decomposition of azo compounds much more than ERG's do. Since the radical-stabilizing power of ERG's is not generally inferior to that of EWG's (cf. Me, OMe, and COOEt, last line), it is differential stabilization of the TS only, and not that of the product radicals, that causes the effects seen here and in Table III.

In what other ways do the requirements imposed by eq 5 and 6 on the developing radical R differ? Looking first

(28) (a) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); (b) D. M. Golden and S. W. Benson, *ibid.*, **69**, 125 (1969); (c) K. W. Egger and A. T. Cocks, *Helv. Chim. Acta*, **56**, 1516 (1973).

(29) Based on disparate values of SE for X = Ac of 6,^{30a} 7,^{30b} 12,^{28a} and 13^{30c} (average = 9.5), taking a lower value for X = COOEt.^{30d}

(30) (a) K. D. King, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **92**, 5541 (1970); J. B. Cumming and P. Kebarle, *ibid.*, **99**, 5818 (1977); (c) A. T. Cocks and K. W. Egger, *J. Chem. Soc., Perkin Trans. 2*, 197, 199 (1973); (d) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

(31) Calculated from SE's of XCH₂ assuming an increment per CH₂ of 3 kcal/mol for the moderately stabilized α -carbonyl radical and 2 kcal/mol for the highly stabilized benzyl radical (note that using 3 kcal/mol for benzyl would strengthen my argument). Thus the ΔS^\ddagger 's per methyl in the series of radicals Me, Et, *i*-Pr, and *t*-Bu are 6, 3, 3,²⁸ for the pair AcCH₂, AcCHMe, 4,^{30b} and for HCOCH₂, HCOCHMe, 3.^{30b}

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

(21) (a) C. Ruchardt and H. Bock, *Chem. Ber.*, **104**, 577 (1971); (b) C. Ruchardt and I. Mayer-Ruthardt, *ibid.*, **104**, 593 (1971); (c) C. Ruchardt and R. Pantke, *ibid.*, **106**, 2542 (1973).

(22) G. Jabuscato and T. T. Tidwell, *J. Am. Chem. Soc.*, **94**, 672 (1972).

(23) S. Ichi, K. A. Kandil, C. Thankachan, and T. T. Tidwell, *Can. J. Chem.*, **53**, 979 (1975).

(24) R. J. Crawford and M. Ohno, *Can. J. Chem.*, **52**, 3134 (1974).

(25) M. Prochazka, O. Ryba, and D. Lim, *Collect. Czech. Chem. Commun.*, **36**, 2640 (1971).

(26) D. S. Malament, *Isr. J. Chem.*, **11**, 819 (1973).

(27) J. W. Timberlake, A. W. Garner, and M. L. Hodges, *Tetrahedron Lett.*, 309 (1973).

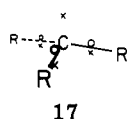
Table IV. Azo Decomposition

$$X-\text{N}=\text{N}-X$$

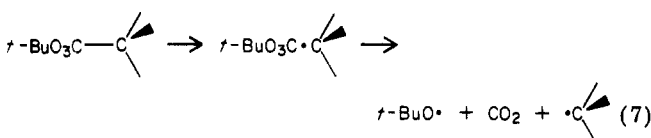
X	Me	OMe	SMe	COOEt	Ph	H
relative rate ²⁷	1	10.5	1.3×10^7	2.6×10^5	4×10^5	1.8×10^{-3}
SE ^a for XCH ₂ ·	6 ²⁸	10 ^{b, 28b}		ca. 9 ²⁹	19 ²⁸	0 ²⁸
SE ^a for XCM ₂ ·	12 ^{28b, c}	14 ^{b, 28b}		ca. 14 ³¹	ca. 23 ³¹	9 ²⁸

^a Based on bond dissociation energies of R-H, assuming that CH₃· has zero stabilization energy (SE). ^b Assuming the same SE as for X = OH.

at peresters (eq 5), we see that R begins as saturated tetravalent carbon and changes to a tetravalent seven-valence-electron form 10a and then to the trivalent seven-electron radical R. The Linnett structure for such a radical is 17.¹⁸ The central carbon atom is not planar, but

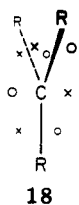


a flattened pyramid, and out-of-plane bending is easier than normal because the three bonds are slightly L-strained. This shape arises because the four-electron spin set is a tetrahedron, and the three-electron spin set is an equilateral triangle, both centered on the nucleus. It is in accord with the stabilities of bridgehead radicals, as in Table II, and with physical evidence.¹¹ The significant thing here is that the shape of the array in R of the central carbon with its three attached groups is the same in 10a as in R, so that the geometry of R changes along the RC smoothly from tetrahedral to flattened pyramidal as in eq 7. This is a least-motion process and explains why per-

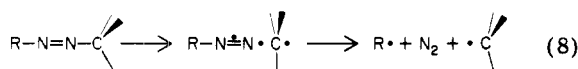


ester thermolysis (with the exception noted earlier of the electronic effects of EWG) obeys the BEPH principle.

However, the developing radical R in eq 6, the azo case, undergoes geometric changes significantly different from those in eq 5. It begins as saturated tetravalent carbon and changes to a tetravalent eight-valence-electron form with two electrons not in the same orbital and then to the radical R. The Linnett structure for the central carbon atom of group R in 16a is the trigonal bipyramid 18.¹⁷⁻¹⁹



The most important attribute of this atom is that it is planar. This shape is most stable because it has the two tetrahedral spin sets arranged for the lowest possible L-strain. The geometry of R, then, does not change smoothly along the RC of eq 6 but proceeds from tetrahedral to planar and then back to flattened pyramidal, as shown in eq 8. This is a non-least-motion process and consequently



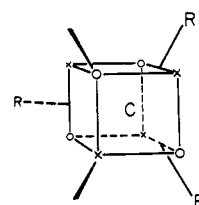
susceptible to anti-BEPH effects if any constraint exists on planarization of R in 16a that does not affect either the starting compound or the radical R. It is the obligatory planarization of the more advanced departing radical

Table V. Bridgehead Effects in Homolyses: Perester vs. Azo Relative Rates³⁴

	t-Bu	Ad	(222)	(221)	t-Bu/ (221)
RCO ₃ +	1	1.4	0.10	0.0014	700
RN=N+	1	0.044	0.021	0.0047	200
RN=NR	1	4×10^{-4}	5×10^{-5}	3×10^{-6}	3×10^5

center that is responsible for the bridgehead azo anomaly.

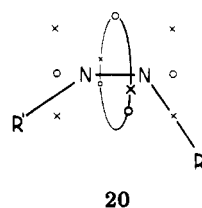
There is another possible shape for R in 16a, in which the central carbon atom is not coplanar with the attached groups, namely, 19.¹⁹ It suffers, however, from $3 \times 70.5^\circ$



L-strain, much more than that in 18, $3 \times 40^\circ$. The energy cost of 19 over 18 with three alkyl groups attached is about 16 kcal/mol,¹⁹ which is remarkably close to the E_a price paid by azoadamantane over azoisobutane.

The idea that the more advanced departing radical in azo pyrolyses, but not the carbon radical in perester thermolyses, must experience a temporary planarity was proposed by Ruchardt to explain the striking observation that symmetrical cycloalkyl azo compounds, but not *tert*-butyl peresters of cycloalkyl carboxylic acids, exhibited a variation in rate vs. ring size similar to that found in the solvolysis of cycloalkyl chlorides.

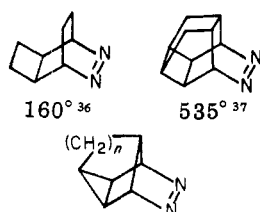
Although the asymmetry in azo TS's is large, it is not complete. It can be seen from Table V (in which the peresters are presented as least-motion controls) that although the first bridgehead substituent (in place of *t*-Bu) evokes a much smaller rate retardation than the second, its effect is still significant for all three bicyclic species. Comparison with the perester series, in which the retardations are probably a manifestation of product development control, makes it seem likely that the effect with the bicyclo-N=N-*t*-Bu series has, at least in part, a different cause; cf. especially the adamantyl column. This can be understood from the full Linnett array around the nitrogens in 15, which is shown as structure 20.³⁵ The less



(33) J. Bonnekessel and C. Ruchardt, *Chem. Ber.*, **106**, 2890 (1973).

(34) A. Oberlinner and C. Ruchardt, *Tetrahedron Lett.*, 4685 (1969); V. Golzke, F. Groeger, A. Oberlinner, and C. Ruchardt, *Nouv. J. Chim.* **2**, 169 (1978).

Table VI. Strained but Stable Azo Compounds



n	no link	0	1	2	3
relative rate ³⁸	2.4×10^{10}		1.0	5.7×10^7	2.1×10^{10}
E_a (kcal/mol) ³⁸	18	37 ³⁹	37	23	20

advanced leaving group R' , which has hitherto received scant attention, is now seen to be bonded to N_2 by a two-electron bond that suffers from 55° primary L-strain, which weakens the bond by about 4–5 kcal/mol.³¹ Associated with this is secondary L-strain within the attached groups, which will be greater the more constrained they are from readjusting their positions to minimize primary L-strain. Secondary L-strains of about 1.5–3 kcal/mol are needed to explain the data. These are reasonable values.¹⁹

Several other important and hitherto unexplained phenomena can be rationalized through the previous discussion. The first of these is displayed in Table VI. One of the most logical and well-exemplified corollaries of the BEPH principle is that compounds react faster, the higher their GS energy, provided the products are not of correspondingly high energy. Therefore, one would be on solid ground in predicting that an increase in GS strain of azo compounds should cause an increase in decomposition rate. A good example is the series $RCMe_2N=NCMe_2R$, whose relative rates vs. R are the following: Me, 1; *t*-Bu, 5.3; neopentyl, 247.⁴⁰ These results can be quantitatively accounted for by GS strain.⁴¹ Many similar cases could be cited.⁴²

Yet the data in Table VI show exactly the opposite trend; the higher the GS strain, the greater the stability. The magnitude of the effects in these highly strained compounds is amazing, especially since loss of the nitrogen bridge undoubtedly relieves much of the strain. These facts, however, are easily understood from eq 8. As the bicyclic systems are tied back tighter and tighter, although their GS strain goes up, their TS strain goes up even faster because planarization of the departing carbon atom is restrained more and more. Several other similar cases are known.⁴³

The same explanation accounts for Engel's observation that even simple bicyclic azo compounds decompose more slowly than expected on the basis of their ring strain energy.^{42a}

(35) This is the array around two atoms, each with octets, connected by a five-electron bond. See structure 4 in ref 18.

(36) H. Tamida, S. Teratake, Y. Hata, and M. Watanabe, *Tetrahedron Lett.*, 5341 (1969).

(37) N. J. Turro, K. Liu, W. Cherry, J. Liu, and B. Jacobson, *Tetrahedron Lett.*, 555 (1978).

(38) E. L. Allred and A. L. Johnson, *J. Am. Chem. Soc.*, **93**, 1300 (1971).

(39) N. J. Turro, C. A. Renners, W. H. Waddell, and T. J. Katz, *J. Am. Chem. Soc.*, **98**, 4320 (1976); cf. B. M. Trost and R. M. Cory, *ibid.*, **93**, 5573 (1971).

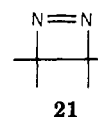
(40) W. Duisman and C. Ruchardt, *Tetrahedron Lett.*, 4517 (1974).

(41) A. W. Garner, J. W. Timberlake, P. S. Engel, and R. A. Melaugh, *J. Am. Chem. Soc.*, **97**, 7377 (1975).

(42) (a) P. S. Engel, *J. Am. Chem. Soc.*, **98**, 1972 (1976); (b) C. Ruchardt, *Forschungsber. Landes Nordrhein-Westfalen*, No. 2471, (1975).

(43) J. A. Berson and R. F. Davis, *J. Am. Chem. Soc.*, **94**, 3658 (1972); M. J. Wyratt and L. A. Paquette, *Tetrahedron Lett.*, 2433 (1974); L. A. Paquette, M. J. Wyratt, H. C. Berk, and R. E. Moerck, *J. Am. Chem. Soc.*, **100**, 5845 (1978); D. W. McNeil, M. E. Kent, E. Hedaya, P. F. D'Angelo, and P. O. Schissel, *ibid.*, **93**, 3817 (1971).

Tetramethyl diazetine 21 is 11 kcal/mol more stable



than predicted from its strain energy.⁴⁴ This case is best interpreted on the basis of bond angles rather than planarization, which is not inhibited here. The internal angle at the departing carbon atom wants to become 90° , and from 20 it can be seen that the angle at the nitrogen bearing the one-electron bond does not change from the GS, but at the other nitrogen the angle grows to about 152° at the MPRC. Taking these things into account, and also the fact that the one-electron bond must be longer than that in the GS, one concludes that a significant increase in I-strain occurs during opening of azo compounds with four-, but not five- or six-membered rings. The idea that the $C-N=N$ angle widens during reaction, based here on structure 20, was anticipated by Ruchardt.⁴⁵ The remarkable stability of dimethyldiazirine ($E_a = 33.1$ vs. $\Delta H^* = 31.7$ for 21) is also apropos.⁴⁶

Bond angles also explain another interesting observation. At 60° , the exo/endo rate ratio for thermolysis of symmetrical 2-phenyl-2-azonorbornane is 471, but that for *tert*-butyl 2-phenylnorbornyl-2-percarboxylate is only 15 (exo and endo refer to the azo and percarboxylate groups).^{42b,47} In the azo compounds, creating a trigonal bipyramid at the norbornyl 2-position pushes an *endo*-azo group into the C-5,C-6 bridge, which is sterically more demanding that it is to push an *exo*-azo group into the C-7 bridge. The effect is much smaller with the percarboxylates because they undergo less flattening at the norbornyl 2-position.

The final example is the subtlest, involving three different effects. The accelerating influence of α -methyl vis-à-vis hydrogen is much less in cyclic than acyclic azo compounds.⁴⁴ An earlier TS for cyclic compounds—anticipated because of greater GS strain—was considered, because this would reduce the expression of methyl's radical-stabilizing power by reducing radical character in the TS, but questioned because α -vinyl and α -phenyl groups labilize cyclic and acyclic azo compounds equally. However, the properties of 16 and 18 support the early TS proposal because (1) the departing carbon atom bears a fractional negative charge at the MPRC which disappears thereafter, so that an earlier TS, i.e., one that is nearer to the MPRC, has more charge which in solution is destabilized by methyl; (2) the three two-electron bonds of the trigonal bipyramid at the MPRC suffer from L-strain, which induces secondary L-strain into methyl but not hydrogen,^{18,19} so that again an earlier TS evokes a destabilizing effect from methyl; (3) phenyl and vinyl are not subject to these two drawbacks because they stabilize carbanions and are almost immune to secondary L-strain.¹⁹

Thus the principal diverse phenomena associated with the pyrolysis of azo compounds can be accounted for by using a single unified mechanistic theory based on Linnert structures. In summary, the theory that has been developed holds that (1) the $R'NN$ angle (see 20) increases from ca. 120° in the GS to ca. 152° in the MPRC, and $R'N$

(44) P. S. Engel, R. A. Hayes, L. Keifer, S. Szilagyi, and J. W. Timberlake, *J. Am. Chem. Soc.*, **100**, 1876 (1978).

(45) W. Duisman and C. Ruchardt, *Tetrahedron Lett.*, 3883 (1976).

(46) G. A. Bottomley and G. L. Nyberg, *Aust. J. Chem.*, **17**, 406 (1964);

H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 3865 (1962).

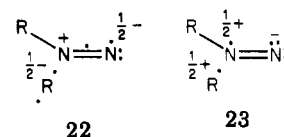
(47) From the data in ref 42b, the compounds cited are the only matched group that can be compared at one temperature without large extrapolation.

L-strain simultaneously increases from 0 to 55° (both remaining unchanged in the radical R'NN•); (2) the NNR angle changes little during reaction, the N-R bond simply lengthening; (3) the more advanced leaving group (sp₃ carbon in the GS) planarizes at the MPRC with concomitant increase of internal bond angles from 109.5° to 120° (see 18 and eq 8) but moves partially back in the product radical 17; (4) this leaving group acquires a transient partial negative charge, and the β-nitrogen a partial positive charge, at the MPRC.

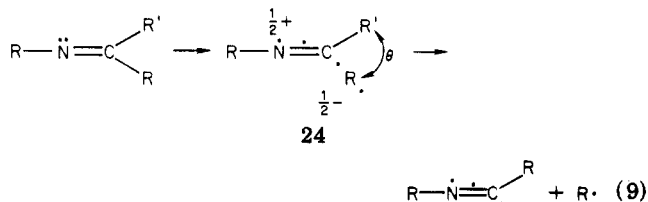
For cases not yet studied, it can therefore be predicted that the reaction will be facilitated by anything that favors these changes, and vice versa. Examples have been given of retardation arising from resistance to planarization, R'NN angle increase and R'N L-strain, and of charge effects. One predicts further that resistance to increase of internal bond angles in the leaving group, e.g., if it is a small ring (including a two-membered ring, i.e., a double bond), will retard reaction.

The above principles should also apply to other homolyses in which the atom β to the primary leaving group is a heteroatom, such as the decomposition of 1,1-diazenes,⁴⁸ in which the best MPRC is 22 rather than 23.

Although the β-situated atom must have unshared electrons in order to have MPRC's like 15 and 22 be fa-



vored, the α atom need not. Thus the above principles should also apply to reaction 9, with the added feature that



angle θ shrinks from about 120° in the GS to about 90° at the MPRC, offering an additional opportunity for testing. Although this reaction should have an E_a ca. 23 kcal/mol higher than that for the correspondingly substituted azo compound,⁴⁹ it might be observable.

(49) Comparing 20 with 24, which has the same array of electrons around the five-electron bond: Δ(bond E) for N=N → N=N exceeds that for N=C → N=C by 13 kcal/mol;⁵⁰ C-R' in 24 has 55° L-strain, 6 kcal/mol (including secondary L-strain);¹⁹ Δ(bond E) for C-C → C-C minus N-C → N-C, 4 kcal/mol,⁵⁰ assuming that a one-electron bond equals half a bond.

(50) R. A. Firestone, *J. Chem. Soc. A*, 1570 (1970), Table 2.

(48) W. D. Hinsberg III and P. B. Dervan, *J. Am. Chem. Soc.*, 101, 6142 (1979); P. G. Schultz and P. B. Dervan, *ibid.*, 102, 878 (1980).

Conformational Effects on Tetraalkylhydrazine Nitrogen-15 Nuclear Magnetic Resonance Chemical Shifts

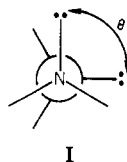
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¹⁵N NMR chemical shifts are reported for 22 tetraalkylhydrazines. For seven acyclic compounds, a plot of δ_N vs. δ_C (¹³C NMR shift at CH for the hydrocarbon analogue of the hydrazine, with N replaced by CH) is a fairly good straight line: δ_N = 1.98δ_C - 67.5₈ (r = 0.99, average deviation 0.8 ppm). Cyclic hydrazines, especially those which have the lone pair-lone pair dihedral angle held near 180 or 0°, show considerable deviations from this line. It is suggested that the amount of flattening at nitrogen has a significant effect on δ_N.

We report the ¹⁵N NMR chemical shifts (δ_N values) of several tetraalkylhydrazines in this paper. Lichter and Roberts¹ have previously discussed δ_N values for tetramethylhydrazine and several less alkylated hydrazines, but we were interested in determining whether δ_N is sensitive to the lone pair-lone pair dihedral angle θ (see I). Acyclic



hydrazines electronically prefer, and exist in, θ ≈ 90° conformations,² but the steric effects accompanying in-

corporation of the hydrazine unit into cyclic structures cause cyclic tetraalkylhydrazines to assume conformations with θ varying between 0 and 180°, as has been demonstrated by studies employing photoelectron spectroscopy (PES),^{3,4} low-temperature ¹³C NMR⁵ spectroscopy, and X-ray crystallography.⁶ The compounds studied here were

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(5) (a) Nelsen, S. F.; Weisman, G. R. *J. Am. Chem. Soc.* 1976, 98, 1842. (b) Nelsen, S. F.; Weisman, G. R. *Ibid.* 1976, 98, 3281. (c) Weisman, G. R.; Nelsen, S. F.; *Ibid.* 1976, 98, 7007.

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