carbon atoms. This high s character is *consistent* with the observed shortness of the bond. Conversely, one might ask what happens to the hybrids if the bridge–bridgehead bond is artificially lengthened, say, to the distance observed in III, by moving the $C_8Cl_1Cl_2$ moiety and adjusting its bond lengths and angles to match those in III, with all other atoms kept in their original positions. Clearly, if this distortion resulted in hybrids similar to those in III, we would then have an equally *consistent* basis for arguing that the bridge–bridgehead bond should have a *normal* length. Fortunately, such a circularity does not arise since calculations on III with the distorted geometry just described lead only to small changes in the s content of the hybrids. Correspondingly, the hybrids of III are not strongly affected when a calculation is carried out using the geometry of the 1,1-dichlorocyclopropane moiety of I. Thus, the difference in C–C bond lengths in I and III reflects the intrinsic difference in the types of hybridization in the two systems.

The other bridgehead bonds in I also deserve some comment. The side bond in the five-membered ring (C_1–C_2) is almost as short (1.483 ± 0.012 Å) as the bridge–bridgehead bond. The key to understanding the C–C_2 bond length lies in noting the similarity of its $sp^{1.73}$ bridgehead hybrid (the C_2 hybrid is $sp^{2.83}$) and that found for the bridgehead C–H bond in [1.1.0]bicyclobutane ($sp^{1.58}$).[20] The latter C–H bond has been referred to as acetylenic, and is noted for its acidic nature.[10,18,21] Therefore it is not surprising that the C_1–C_2 bond length in I approaches that found for the single bond of methylacetylene (1.459 Å),[22] the bond hybrids for the latter molecule being $sp^{1.10}$ ($-C\equiv$) and $sp^{2.78}$ (CH_3-).[12a]

As noted above, the bridgehead–bridgehead bond is formed from two essentially pure p orbitals ($sp^{29.4}$). This bond is probably the bond least amenable to a simple analysis because it is the one most subject to the constraints imposed by the other bridgehead bonds. It is interesting to note that it is considerably longer (1.572 ± 0.015 Å) than its counterpart in [1.1.0]bicyclobutane (1.497 ± 0.003 Å),[23] also formed from p hybrids.[10a,18] Part of the difference may lie in the fact that the p orbitals in [1.1.0]bicyclobutane deviate from the bridgehead–bridgehead vector by $\sim$33°, compared to only a 21° deviation for I. A similar analysis in terms of hybrid orientation has been invoked by Bent[9] to account for the different C–C bond lengths in cyclopropane (1.510 Å)[17a] and cyclobutane (1.584 Å).[24]

The side bond of I in the five-membered ring seems to be the most normal. The slight shortening relative to cyclobutane is presumably related to the s content ($sp^{2.28}$) of the bridgehead hybrid.

In conclusion it should be noted that while the four C–C *interatomic vectors* at each bridgehead do indeed lie on one side of a plane, the same is not true for the corresponding *bond hybrids*. The six interhybrid angles at a given bridgehead range from 101 to 116°,[13b] leading to a model more closely akin to that expected for a four-coordinate carbon atom than one might infer from simply connecting atomic centers.

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(20) This is nearly identical with the INDO value reported in ref 10a.

(21) K. B. Wiberg, G. M. Lampman, R. P. Cuila, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, 21, 2749 (1965).

(22) C. C. Costain, *J. Chem. Phys.*, 29, 864 (1958).

(23) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *ibid.*, 50, 1976 (1969).

(24) A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, 15, 711 (1961).

Mechanism of Azoalkane Thermolysis. Concerted or Nonconcerted?

Robert J. Crawford* and Kunihiko Takagi

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada.

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Abstract: The synthesis and gas-phase thermolysis of the unsymmetrical azo compounds, methylazo-3-propene (**6**), 1-propylazo-3′-propene (**7**), and *tert*-butylazo-3-propene (**8**), are described. The nitric oxide inhibited rates of thermolysis of **6**, **7**, and **8** at 122.3° are compared with the rate of thermolysis of azo-3,3′-propene (**5**). It is concluded that the azoalkanes undergo thermolysis in the gas phase to produce two fragments in the rate-determining step. The secondary deuterium kinetic isotope effect of methylazo-3-propene-*3,3-d*$_2$ was determined, and the value obtained, $k_H/k_D = 1.28$ at 126.0° ($\Delta\Delta G^{\ddagger}$ per deuterium, 98 ± 15 cal mol^{-1}), is consistent with the formation of two fragments for both **5** and **6**.

Azoalkanes have been used for many years as a convenient source of alkyl radicals, but there remains some doubt as to the nature of the initial mechanistic step involved in their thermolysis. The earliest work addressed directly to this matter was that of Ramsperger[1] who compared the activation parameters of **1**, **2**, and **3** and was led to conclude that "The heat of activation of **3** is intermediate between that for dimethyl diimide (**1**) and di-isopropyl diimide (**2**). . . If the reaction occurs by the simultaneous rupture of both bonds, then we may expect an intermediate heat of activation, and this is the experimental result." The activation energy is 47.5 kcal mol^{-1} for **3**, being slightly larger than the arithmetic mean of the then accepted values of 51.2 and 40.9 kcal mol^{-1} for **1** and **2**. Subsequent

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

investigations have revealed that azomethane produces large quantities of methane upon thermolysis and that chain-induced decomposition tends to lower the activation energy below that of the true unimolecular rate.[2] The validity of the activation energy for **2** has similarly been questioned since (a) it is susceptible to tautomerism, and (b) having a tertiary hydrogen it is likely to undergo chain-induced decomposition. This suspicion is enhanced when it is noticed that its activation energy is lower than that of 2,2′-azoisobutane (**4**)[3] and that it does not fit on the Polanyi plot[4] observed for those azoalkanes wherein chain-induced decomposition has been corrected for in obtaining the activation parameters. The activation energy for **2** that would be expected from the Polanyi plot is 46 ± 1 kcal mol^{-1}, a value which if observed would completely reverse Ramsperger's conclusion.

Initially the thermolyses of meta- and para-substituted phenylazotriphenylmethanes were interpreted to proceed *via* a three fragment forming homolysis,[5] but the elegant work of Pryor and Smith has shown that cage effects were responsible for the misleading differences observed in the earlier work,[6] and that the phenyldiimide radical is a species of finite lifetime in solution. This has been supported by the photochemical racemization of chiral azo compounds wherein the phenyldiimide radical is the most reasonable species for the photodissociation.[7] The immense difference in stability between the phenyldiazonium cation and the methyldiazonium cation is such that one is hesitant to translate evidence for the existence of the phenyldiimide radical to that of a methyldiimide radical.

Steric factors play an important role in the thermolysis of hindered and cyclic azo compounds.[8] Overberger and coworkers[8a] using a series of azonitriles observed that substitution at the α carbon gave an appreciable change in rate (see Table I). Similarly Cohen, *et al.*,[9] have observed that in changing the alkyl group in the symmetrical azoalkanes ($(C_6H_5CHRN{=})_2$) from methyl to ethyl to isobutyl the thermolysis rate changes from 5.45×10^{-5} sec^{-1} to 2.35×10^{-5} sec^{-1} to 7.60×10^{-5} sec^{-1} at 100.4°. The subtle nature of the steric effects is well demonstrated by the difference in rate observed for disastereomeric azo compounds as demonstrated in Table II. Any kinetic test of mechanism must make allowance for these factors.

Table I. Rate Constants for the Thermolysis of α-Substituted Azoalkanes, $C_6H_5RR'CN{—}NCRR'C_6H_5$, in Diphenyl Ether at 120° [a]

R	R′	10^4k, sec^{-1}	Rel rate
CH_3	CH_3	1.06	1.00
C_2H_5	C_2H_5	0.78	0.73
CH_3	$(CH_3)_2CHCH_2$	8.51	8.03

[a] Taken from C. G. Overberger and A. V. Di Guilo, *J. Amer. Chem. Soc.*, **81**, 2154 (1959).

Table II. Comparison of Rate Constants for *meso*- and *rac*-Azoalkanes, RR′R′′CN=NCR′′R′R

R	R′	R′′	*T*, °C	Ratio of rates
Benzyl	Phenyl	H	106	1.17[a]
Neopentyl	Methyl	CN	80.2	1.16[b]
Vinyl	Methyl	H	125	1.20[c]
tert-Butyl	Methyl	CN	79.9	1.42[b]
Cyclopropyl	Methyl	CN	44.2	1.12[b]
Isobutyl	Methyl	CN	69.9	1.46[b]

[a] S. E. Scheppele and S. Seltzer, *J. Amer. Chem. Soc.*, **90**, 358 (1968). [b] See ref 8a. [c] B. Strehlke, Ph.D. Thesis, University of Alberta, 1971.

$$R{—}N{=}N{—}R' \longrightarrow R\cdot + N_2 + \cdot R' \qquad (1)$$

There are several other studies which support eq 1 as the rate-determining step, the most noteworthy of which are the secondary deuterium kinetic isotope effect studies of Seltzer and coworkers[10] on the system $R = R' = C_6H_5CH(CH_3)$–. However, when unsymmetrical azo compounds such as $R = C_6H_5CH(CH_3)$–, $R' = CH_3$–, and $(CH_3)_2CH$– were studied they found definite evidence to support the two-step process (eq 2).

$$R{—}N{=}N{—}R' \longrightarrow R\cdot + \cdot N{=}N{—}R' \longrightarrow R\cdot + N_2 + \cdot R' \qquad (2)$$

More recently Rüchardt[11] has published work indicative of symmetrical cleavage (eq 1) while Benson and O'Neal have concluded that eq 2 best describes the mechanism for all of the azoalkanes examined in the gas phase.[12]

It has been demonstrated[4d] that the gas-phase thermolysis of symmetrical azoalkanes gives a Polanyi plot described by the equation $E_a = 0.996D(\text{R–H}) - 48.4$. The slope, α, indicates the sensitivity of structural changes in the alkyl radical(s) of the azoalkane as compared with the radical produced upon the dissociation of the R–H bond in the corresponding hydrocarbon. If the stepwise mechanism applies then α = 0.996 and structural changes in the stability of the radical are equally reflected in the C–N bond of the azoalkane. As a consequence thermochemical data are capable of predicting the activation energies.[12] For unsymmetrical azoalkanes (R—N=N—R′) we expect that if the nonconcerted, stepwise mechanism, eq 2, holds, then *D*(R–H) of the Polanyi equation is the bond dissociation energy of the weaker carbon–hydrogen bond of R–H and R′–H. It may be that the near unity

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(2) C. Steel and A. F. Trotman-Dickenson, *J. Chem. Soc.*, **75** (1959); H. A. Taylor and F. P. Jahn, *J. Chem. Phys.*, 7, 470 (1939).

(3) J. B. Levy and B. K. W. Copeland, *J. Amer. Chem. Soc.*, **82**, 5314 (1960).

(4) (a) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938); (b) A. F. Trotman-Dickenson, "Free Radicals," Wiley, New York, N. Y., 1959, p 77; (c) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); (d) B. H. Al-Sader and R. J. Crawford, *Can. J. Chem.*, **48**, 2745 (1970).

(5) S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, **75**, 5504 (1953); S. Solomon, C. H. Wang, and S. G. Cohen, *ibid.*, **79**, 4104 (1957).

(6) W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967); **92**, 5403 (1970).

(7) N. A. Porter, M. E. Landis, and L. J. Marnott, *ibid.*, **93**, 795 (1971).

(8) (a) C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *ibid.*, 71, 2261 (1949); C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 2618 (1951); C. G. Overberger, H. Biltech, A. B. Finestone, J. Litker, and J. Herbert, *ibid.*, **75**, 2078 (1953); C. G. Overberger, W. H. Hale, M. B. Berenbaum, and A. B. Finestone, *ibid.*, **76**, 6185 (1954); (b) M. Prochazka, O. Ryba, and D. Lim, *Collect. Czech. Chem. Commun.*, 36, 2640 (1971).

(9) S. G. Cohen, S. J. Groszos, and D. B. Sparrow, *J. Amer. Chem. Soc.*, 72, 2078 (1950).

(10) S. Seltzer, *ibid.*, **83**, 2625 (1961); **85**, 14 (1963); S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965).

(11) C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

(12) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 21, 31 (1970).

Table III. Product Composition from the Thermolysis of Methylazo-3-propene (**6**) (57 Torr) at 131.6°

Completion, %	Product composition relative to nitrogen formed, %: Methane	1-Butene	1,5-Hexadiene	Azomethane	Ethane	Propene	Methyl[b] radicals recovered, %	Allyl[c] radicals recovered, %
12.2	30.8	35.7	19.4	4.5	0.9	0.7	78	75
30.3[a]	36.0	33.3	18.7	4.6	0.7	0.7	80	72
38.5[a]	35.3	31.0	18.0	4.4	0.7	0.8	77	68
48.3	34.5	27.1	16.5	3.8	0.7	0.7	72	61

[a] 0.4% of *n*-pentane also identified as a component of this run. [b] % methyl radicals recovered = % methane + % 1-butene + 2(% *n*-pentane + % azomethane + % ethane). [c] Allyl radicals recovered = % 1-butene + % propene + % *n*-pentane + 2(% 1,5-hexadiene).

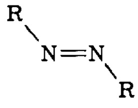
value of the slope is fortuitous and that a concerted process wherein two carbon–nitrogen bonds are breaking is described by the equation $E_a = 0.498D(\text{R–H}) + 0.498D(\text{R–H}) - 48.4$ for the symmetrical azoalkanes, and results in the same plot. The symmetrical azoalkanes alone are not readily capable of defining the mechanism. Thus for the concerted process a generalized form of the Polanyi equation such as (3), wherein both carbon–nitrogen bond[13] dissociation energies are considered, may be being observed.

$$E_a = \alpha D(R\text{–H}) + \alpha' D(R'\text{–H}) - C \qquad (3)$$

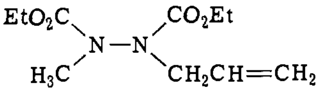
In choosing to examine this reaction we set forth some specific requirements of the compounds to be studied: (i) that the difference in bond dissociation energies of the R–H and R′–H used in the unsymmetrical compounds (R—N═N—R′) be kept as large as is practical; (ii) that the compounds must be volatile enough to conveniently handle on a vacuum line; (iii) that chain-induced decomposition must be minimized so that true unimolecular thermolysis data are obtained; (iv) allowance must be made for steric effects; and (v) that the corresponding symmetrical azo compounds (R—N═N—R and R′—N═N—R′) be such that their kinetic parameters are readily available. The detailed study of Forst and Rice[14] on the use of nitric oxide as an inhibitor in azomethane thermolysis lead us to this method for the study of compounds **6**, **7**, and **8**.

Results and Discussion

Synthesis. The azo compounds **6**, **7**, and **8** were prepared by the oxidation of the corresponding hydrazines which in turn were prepared by the hydrolysis of the corresponding dialkyl bicarbamates. Because the kinetics were studied at low conversion it was necessary to have no contamination of the reactant with other azo compounds. This was ensured for **6** by first monoallylating diethyl bicarbamate and carefully separating it from traces of the diallylated material, and then by methylating to give **9**. The bicarbamate,



1, $R = R' = CH_3–$
2, $R = R' = (CH_3)_2CH–$
3, $R = CH_3–; R' = (CH_3)_2CH–$
4, $R = R' = (CH_3)_3C–$
5, $R = R' = CH_2{=}CHCH_2–$
6, $R = CH_3–; R' = CH_2{=}CHCH_2–$
7, $R = n\text{-}C_3H_7–; R' = CH_2{=}CHCH_2–$
8, $R = (CH_3)_3C–; R' = CH_2{=}CHCH_2–$



9

9, was also synthesized by reversing the order of introduction of the alkyl groups. All of the azo compounds were carefully purified by preparative gas chromatography followed by trap-to-trap distillation to remove any high molecular weight impurity which might be slowly eluting from the column, Mass spectrometry and gas chromatography were used to ensure that there was no **1** or **5** in **6**. In the case of **8** the *tert*-butylhydrazine was first synthesized by the procedure of Smith, *et al.*,[15] and then allowed to react with methyl chloroformate followed by allylation to give the bicarbamate.

Products of the Noninhibited Thermolysis of Methylazo-3-propene (6) and *tert*-Butylazo-3-propene (8). Samples of **6** and **8** were carefully degassed in breakseals on a vacuum line before being transferred to a thermostated oil bath. The products were identified by their gc retention times and by their fragmentation patterns. The results at varying percentages of completion are given in Tables III and IV. The fourth largest peak in the gc resulting from the thermolysis of **6** was not readily identified and so a small sample was collected and its exact mass measured as 58.0530, corresponding to $C_2H_6N_2$. The retention time proved to be identical with that of an authentic sample of azomethane. In addition to those indicated in Table III numerous small fractions corresponding to C_8–C_{10} hydrocarbons were observed by gc. These were too small in quantity to be properly identified. The large amounts of methane produced suggest that there is chain-induced decomposition of **6**. Besides abstracting hydrogen the methyl radicals produced can also add to the nitrogen–nitrogen and carbon–carbon double bonds to give radicals **10** and **11**. These reactions are of lesser importance to the allyl radicals which mostly end up as the dimer 1,5-hexadiene.[4] The radical **10** can ac-

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(13) While such a relationship may not hold exactly[4b] it does allow a useful model for discussion. It is a more generalized statement for Ramsperger's criteria wherein $\alpha = \alpha'$ and is useful in that we can test for varying degrees of concertedness, *e.g.*, where $\alpha + \alpha' = 1.0$ as in the azoalkanes then we may test for $\alpha = 0.8$, $\alpha' = 0.2$. The equation for the stepwise process is produced when $\alpha' = 0$, since α' is associated with the stronger of the carbon–nitrogen bonds in R′N═NR.

(14) (a) W. Forst and O. K. Rice, *Can. J. Chem.*, 41, 562 (1963). (b) A study of the thermolysis of azomethane-d_6 by Do-Reng Chang and O. K. Rice, *Int. J. Chem. Kinet.*, 1, 171 (1969), suggests that the rate constant obtained by extrapolation to zero nitric oxide pressure may not be the true unimolecular rate constant because of the amount of methane-d_4 produced in the presence of low concentrations of nitric oxide. In our studies, see the Experimental Section, no hydrocarbons were detected in the nitric oxide inhibited runs. This is probably a consequence of the lower temperatures used herein, 130° as compared with 275°. Alkyl nitroso compounds are known to undergo homolysis at higher temperatures.

(15) P. A. S. Smith, J. M. Clegg, and J. Lakritz, *J. Org. Chem.*, 23, 1595 (1958).

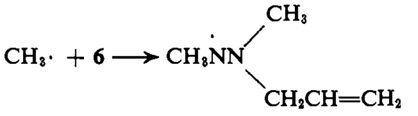
Table IV. Product Composition from the Thermolysis of *tert*-Butylazo-3-propene (**8**) at 122.3°

Completion, %	Product composition relative to nitrogen formed, %: Isobutane	Isobutene	1,5-Hexadiene	4,4-Dimethyl-1-pentene	2,2,3,3-Tetramethylbutane	Allyl[a] radicals recovd, %	*tert*-Butyl[b] radicals recovd, %
21.8	49.2	11.6	20.9	44.6	2.7	86	103
40.0	33.1	9.5	20.0	43.8	2.7	84	92
52.7	30.0	7.8	18.6	40.8	2.7	78	84
63.5	30.3	8.2	19.3	40.1	2.8	79	83
71.0	30.1	8.3	20.1	47.1	3.1	87	86

[a] % allyl radicals recovered = % 4,4-dimethyl-1-pentene + 2(% 1,5-hexadiene). [b] % *tert*-butyl radicals recovered = % isobutane + % isobutene + % 4,4-dimethyl-1-pentene + 2(% 2,2,3,3-tetramethylbutane).

$$CH_3\cdot + \mathbf{6} \longrightarrow CH_3N{=}NCH_2\dot{C}HCH_2CH_3 \qquad (4)$$

10



$$CH_3\cdot + \mathbf{6} \longrightarrow CH_3\dot{N}N(CH_3)(CH_2CH{=}CH_2) \qquad (5)$$

11

count for some of the 1-butene produced and β cleavage of the allyl to nitrogen bond of **11** presents a reasonable explanation for the production of azomethane. Methane production undoubtedly comes from reactions such as 6 and 7. Since the rate of thermolysis of **6** was followed by the rate of formation of

$$CH_3\cdot + \mathbf{6} \longrightarrow CH_4 + \cdot CH_2N{=}NCH_2CHCH_2 \qquad (6)$$

12

$$CH_3\cdot + \mathbf{6} \longrightarrow CH_4 + CH_3N{=}NCHCH{=}CH_2 \qquad (7)$$

13

nitrogen reactions 4–7 will affect the rate only if the ultimate fate of the radicals **10**–**13** is the formation of nitrogen. The ratio of the noninhibited rate constant to the inhibited rate constant is *ca.* 1.6 (see below), suggesting that about 40% of the nitrogen produced comes from radicals such as **10**, **12**, and **13**. The reactions which most probably produce nitrogen and which are part of radical chains and increase the rate of thermolysis are reactions 8, 10, and 11. Reactions 12 and 13 do

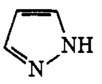
$$\mathbf{12} \longrightarrow CH_2{:} + N_2 + CH_2{=}CHCH_2\cdot \qquad (8)$$

$$\mathbf{12} \longrightarrow CH_2N_2 + CH_2{=}CHCH_2\cdot \qquad (9)^{16}$$

$$CH_2N_2 \longrightarrow CH_2{:} + N_2 \qquad (10)$$

$$\mathbf{13} \longrightarrow CH_3\cdot + N_2 + {:}CHCH{=}CH_2 \qquad (11)$$

$$\mathbf{11} \longrightarrow CH_3\cdot + CH_2{=}CHCHN_2 \qquad (12)$$

$$CH_2{=}CHCHN_2 \longrightarrow$$  $$(13)$$

not produce nitrogen, but the vinyldiazomethane may thermolyze to nitrogen and allylidene, or cyclize to pyrazole;[17] however, pyrazole was not detected. The material balance with respect to the allyl and methyl fragments is indicated in the final column of Table III.

No 2,2′-azoisobutane was detected in the thermolysis of **8**, suggesting that the bulky *tert*-butyl radicals are not as facile at adding to the azo nitrogens as are the methyl radicals. Since the rate of thermolysis of 2,2′-azoisobutane was unaffected by the presence of isobutane[3] and the photolysis of di-*tert*-butyl ketone was unaffected by the presence of nitric oxide,[18] the hydrogen abstraction, reaction 14, by *tert*-butyl radicals seems to be of little importance. The fact that the amount of isobutane is eight times that of isobutene may arise from the abstraction of allylic hydrogens by *tert*-butyl radicals, reaction 15, or by a process wherein isobutane is formed at the expense of isobutene,[3] *e.g.*, reaction 15.

$$(CH_3)_3C\cdot + \mathbf{8} \longrightarrow (CH_3)_3CH + \cdot CH_2(CH_3)_2CN{=}NR \qquad (14)$$

$$(CH_3)_3C\cdot + (CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_3CH + \cdot CH_2C(CH_3)CH_2 \qquad (15)$$

$$\cdot CH_2C(CH_3)CH_2 \longrightarrow \text{dimer} \qquad (16)$$

If reaction 14 is not important, then the ratio of the rate constants for the disproportionation reaction to the combination reaction, k_a/k_c, can be calculated according to expression 17. The values obtained are 5

$$(CH_3)_3CC(CH_3)_3 \xleftarrow{k_c} 2(CH_3)_3C\cdot \xrightarrow{k_a} (CH_3)_3CH + (CH_3)_2C{=}CH_2$$

$$\frac{k_{14}}{k_{15}} = \frac{1}{2}\frac{\text{yield of isobutene}}{\text{yield of 2,2,3,3-tetramethylbutane}} \qquad (17)$$

at low conversion and 3 at high conversion, which compare favorably with the value of 4.6 obtained from the photolysis of di-*tert*-butyl ketone[18] and from the mercury-photosensitized hydrogenation of isobutene.[19] The material balance and yields from **8** are listed in Table IV.

Kinetics of the Noninhibited Thermolysis of 6. The rate of the noninhibited thermolysis of methylazo-3-propene (**6**) was measured by following the increase of pressure with time during the thermolysis, and by measuring the amounts of nitrogen produced. The linearity of the plots of log $(P_\infty - P_t)$ *vs.* time, where P is the pressure, displayed good first-order behavior in spite of the radical chain induced decomposition discussed in the previous section. The activation parameters and rate constants are given in Table V. The rates measured in the static vessel, *via* pressure increase, were carried out at higher temperatures than those in sealed vials, wherein the rate of production of nitrogen was measured. At 131.6° the measured rate *via* the

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(16) Y. Paquin and W. Forst (54th Meeting of the Chemical Institute of Canada, Halifax, Nova Scotia, 1971 Abstract, Phys. IX 3) have shown that diazomethane is produced in the uninhibited thermolysis of azomethane.

(17) C. D. Hurd and S. C. Lui, *J. Amer. Chem. Soc.*, **57**, 2656 (1935); I. Tabushi, K. Takagi, M. Okano, and R. Oda, *Tetrahedron*, 23, 2621 (1967).

(18) J. W. Kraus and J. G. Calvert, *J. Amer. Chem. Soc.*, **79**, 5921 (1957).

(19) A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, New York, N. Y., 1955, p 236.

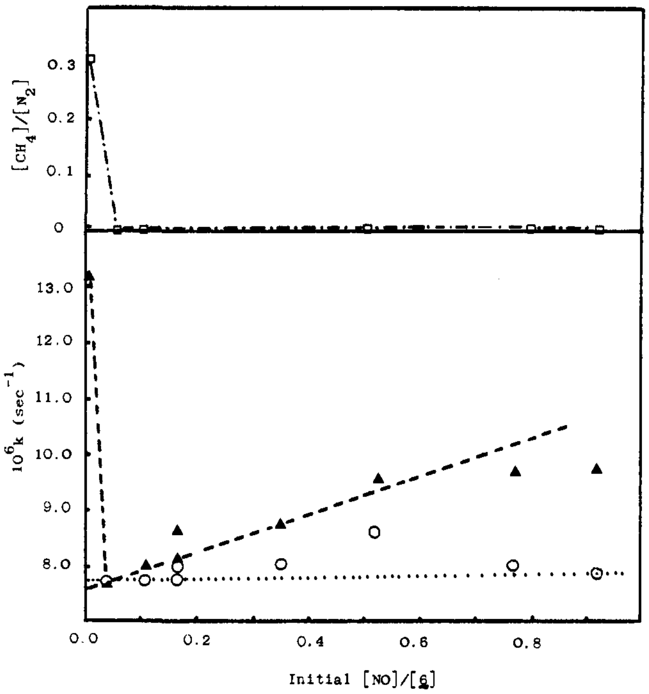

Figure 1. Inhibited thermolysis of **6** at 57 Torr: □, methane yield as a fraction of nitrogen produced; ▲, uncorrected rate constant; ○, corrected rate constant.

Table V. Rate Constants and Activation Parameters for the Uninhibited Thermolysis of Methylazo-3-propene (**6**)

Run no.	Temp, °C	10^4k, sec^{-1}	Activation parameters
1	163.3	5.88	$E_a = 35.4 \pm 0.7$ kcal mol^{-1}
2	169.8	11.10	$\log A = 14.51 \pm 0.32$
3	175.0	18.10	$\Delta S^{\ddagger} = 5.3 \pm 1.5$ eu (at 120°)
4	182.8	33.6	

latter technique is 1.82×10^{-5} sec^{-1} and may be compared to that obtained by extrapolation from the pressure increase technique of 2.57×10^{-5} sec^{-1}.

The rate constant for the noninhibited thermolysis of **8** was obtained by measuring the rate of nitrogen production. At an initial pressure of 46 Torr at 122.3° the rate is 2.78×10^{-4} sec^{-1}.

Inhibition by Nitric Oxide. Evidence was presented in the previous sections to show that there is a chain-induced decomposition component in the thermolysis of **6** and **8** in the absence of inhibitors. Nitric oxide (NO) was found to be an excellent inhibitor in the thermolysis of azoalkanes[14] and as such it was chosen for our study of **6**, **7**, and **8**. While it is believed that reactions between nitric oxide and olefins do not occur[20] Brown[21] has reported that the reaction of nitric oxide with isobutene occurs readily in the presence of traces of nitrogen dioxide (NO_2) such as are usually present in samples of nitric oxide. After careful purification to remove any nitrogen dioxide, control experiments with nitric oxide and 1-butene were carried out, and it was demonstrated that the olefinic double bond did not react at temperatures of 130° or lower.

In order to test the efficiency of nitric oxide as a radical trap a number of mixtures of **6** and nitric oxide were prepared in such a manner that the pressure of **6** was constant at 60 Torr, but the ratio of nitric oxide to **6** was varied from 0.0 to 1.04. The mixtures were then heated to 125.9° for 100 min. At a nitric oxide to azo ratio of 0.06, or greater, less than 0.5% (based on nitrogen produced) of hydrocarbon products could be detected; see Figure 1. The amount of nitrogen formed was at a minimum over the range 0.06–0.22. The amount of **6** recovered was measured by gc and a satisfactory material balance was obtained. The reduction in rate implies the removal of radicals **10**, **12**, and **13** or their precursor the methyl radical. Since the bulk of hydrocarbons in the noninhibited reaction must be due to subsequent reactions of methyl radicals, the drastic reduction by nitric oxide of the yield of hydrocarbons indicates the removal of methyl radicals. The absence of hydrocarbons suggests that the methyl and allyl radicals are removed by the processes 18 and

$$CH_3\cdot + \cdot NO \longrightarrow CH_3NO \qquad (18)$$

19. It is generally appreciated that nitrosoalkanes

$$CH_2{=}CHCH_2\cdot + \cdot NO \longrightarrow CH_2{=}CHCH_2NO \qquad (19)$$

react further with nitric oxide,[21,22] or tautomerize to oximes,[23] or dimerize.[24] The absence of 1-butene rules out any concerted loss of nitrogen from **6**.

Since both **6** and nitric oxide contain nitrogen, and the rate of the inhibited thermolysis with nitric oxide is measured by the rate of formation of nitrogen, then the accelerating effect of nitric oxide, *i.e.*, the rate increase at higher nitric oxide pressures indicated in Figure 1, could be due to the production of nitrogen from either **6** or from the nitric oxide. Experiments with isotopic nitric oxide (^{15}NO, isotopic purity 99.6%) permit a distinction between these two possible modes of nitrogen production. The initial pressure of 58 Torr of **6** (*ca.* 30 μmol in a 16-ml breakseal) was kept constant and the ratio of isotopic nitric oxide to **6** was varied from 0.047 to 0.915. Table VI shows the results obtained from placing each tube in an oil bath for exactly 90 min at 126.35°. The nitrogen produced was first measured volumetrically and then an aliquot was analyzed by mass spectrometry. The rate constant based on total nitrogen produced is indicated as k_1^{tot}. Using mass 28, corresponding to $^{14}N^{14}N$ as the parent peak (100), the relative values for peaks at mass 29 and 30 are listed in Table VI. It is apparent that molecular nitrogen is produced from the nitric oxide. A control experiment excludes the direct isotopic exchange reaction at the reaction temperatures. The value $f_{N_2}{}^6$ is that fraction of the total nitrogen derived from the reactant **6**.[25] We may conclude that

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(20) N. V. Sidgwick, "The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1949, p 213.

(21) J. F. Brown, Jr., *J. Amer. Chem. Soc.*, **79**, 2480 (1957).

(22) E. Bamberger, *Ber.*, **51**, 634 (1918); M. I. Christie, *Proc. Roy. Soc., Ser. A*, **249**, 258 (1959); B. G. Gowenlock and M. J. Healey, *J. Chem. Soc. B*, 1014 (1968).

(23) H. T. J. Chilton and B. G. Gowenlock, *ibid.*, 3232 (1953); B. G. Gowenlock, and J. Trotman, *ibid.*, 4190 (1955); L. Batt and B. G. Gowenlock, *Trans. Faraday Soc.*, **56**, 682 (1960).

(24) J. G. Calvert, S. S. Thomas, and P. L. Hanst, *J. Amer. Chem. Soc.*, **82**, 1 (1960); B. G. Gowenlock and J. Kay, *J. Chem. Soc.*, 2880 (1962).

(25) The natural abundance of $^{15}N^{14}N$ in ordinary nitrogen is 0.738 mol %;[26] thus the contribution from this source is $0.00748P_{28}$ and the fraction of nitrogen, of natural isotopic composition, from **6** is then

$$f_{N_2}{}^6 = \frac{1.0037 + 0.5P_{29}/P_{30}}{1.000 + P_{29}/P_{28} + P_{30}/P_{28}}$$

Table VI. Mass Spectrometric Analysis from the Runs of Methylazo-3-propene (**6**) with ^{15}NO at 126.35° and 57 Torr

$[NO]^0/[\mathbf{6}]^0$	Mass analysis[a] ^{29}R	^{30}R	$f_{N_2}{}^6$	10^6k, sec^{-1} Uncorr	Corr	NO[b] consumed
0.00			1.00	13.2		
0.0407	0.75	0.31	0.996	7.70	7.70	1.0
0.104	1.07	3.61	0.968	8.01	7.77	1.92
0.171	0.97	4.86	0.954	8.19	7.80	1.89
0.172	1.62	7.05	9.932	8.68	8.09	1.78
0.351	1.59	9.69	0.911	8.78	8.01	2.27
0.511	6.31	6.98	0.914	9.61	8.76[c]	2.38
0.779	1.32	20.0	0.832	9.65	8.00	3.02
0.915	1.11	23.6	0.810	9.77	7.88	2.67

[a] ^{29}R and ^{30}R are $10^2 \times {}^{29}p/{}^{28}p$, and $10^2 \times {}^{30}p/{}^{28}p$, respectively. [b] The number of moles of nitric oxide consumed per mole of **6** consumed. [c] Not used in computing the average.

$$^{14}N^{14}N + {}^{15}NO \longrightarrow {}^{14}N^{14}N + {}^{14}NO$$

if the nitric oxide does induce the thermolysis of **6** it is not significantly detected,[27] and that the products of thermolysis of **6** in the presence of nitric oxide are responsible for the increased nitrogen.

Since two radicals (methyl and allyl) are formed per nitrogen molecule produced, a complete removal of the radicals by nitric oxide according to reactions 18 and 19 should lead to the consumption of 2 mol of nitric oxide per mole of nitrogen produced. The amount of ^{15}NO recovered was measured and the quantity consumed was calculated. The results expressed as the number of moles of ^{15}NO consumed per mole of nitrogen produced from **6** are listed in the final column of Table VI. The ratios rise gradually with increasing pressure of nitric oxide, and are similar to the results obtained by Forst and Rice in the thermolysis of azomethane.[14a] The ratios lower than two, in the lower nitric oxide pressure range, require that an inhibitor other than nitric oxide must be present. Nitrosoalkanes are known to act as inhibitors, although less efficiently than does nitric oxide.[28] The values larger than two, at higher pressure, coincide with the formation of nitrogen from ^{15}NO. The formation of nitrogen from nitric oxide has been demonstrated by several workers to arise from a reaction of the latter with nitroso compounds.[14,21,22,29] No dependence upon initial pressure was observed when the nitric oxide and **6** pressure was held constant at 58 Torr ($[NO]/[\mathbf{6}] = 0.211$) and the total pressure was varied over the range of 58–135 Torr by adding xenon, indicating that 58 Torr is above the pressure-sensitive region of the unimolecular decomposition of **6**. Extrapolation to zero nitric oxide concentration gives a rate constant of 7.70×10^{-6} sec^{-1} which compares favorably with the average value of $k_{\mathrm{corr}}{}^6$ of 7.89×10^{-6} sec^{-1}. The rate studies over a range of temperatures were carried out at the optimum nitric oxide:**6** ratio of 1:6. Under these conditions the value of the total nitrogen measured can be used directly to calculate the rates with very little loss of precision, and all of the chain-induced components of the reaction will be removed. Mixtures of **6** (*ca.* 40 Torr) and nitric oxide (6–8 Torr) were allowed to react up to 6% conversion. Rate constants were evaluated from the slopes of the plots of $-\log\,(1 - [N_2]^t/[\mathbf{6}]^0)$ *vs.* time (t); a sample run is given in the Experimental Section. Rate constants at various temperatures are listed in Table VII along with activation parameters.

Table VII. Rate Constants and Activation Parameters for the Thermolysis of **6**, **7**, and **8** in the Presence of ^{15}NO (Total Pressure 50–60 Torr)

Compd	Temp, °C	10^6k, sec^{-1}	Activation parameters
6	109.90	1.27	$E_a = 35.5 \pm 0.7$ kcal mol^{-1}
	115.53	2.27	$\log A = 14.36 \pm 0.38$
	125.92	7.80	$\Delta S^{\ddagger} = 4.6 \pm 1.8$ eu
	129.52	12.2	
7	101.32	1.10	$E_a = 35.6 \pm 0.5$ kcal mol^{-1}
	114.10	5.60	$\log A = 14.80 \pm 0.28$
	126.02	21.1	$\Delta S^{\ddagger} = 6.6 \pm 1.3$ eu
8	80.88	2.13	$E_a = 29.8 \pm 0.3$ kcal mol^{-1}
	90.90	7.27	$\log A = 12.73 \pm 0.26$
	91.50	7.47	$\Delta S^{\ddagger} = -2.8 \pm 1.3$ eu
	106.81	38.9	

Kinetic studies of the inhibited thermolysis of 1-propylazo-3′-propene (**7**) with nitric oxide were carried out in the same manner as those described for **6**. The rate constants and activation parameters are given in Table VII. The values were checked using the mass spectrometric correction and in each case were within experimental error of the result obtained by taking the value of total nitrogen evolved. The thermolysis rate of 3,3′-azo-1-propene (**5**) was unchanged by the addition of nitric oxide indicating that there is no chain component and that the previously obtained data are that of the pure unimolecular thermolysis.[4d]

When *tert*-butylazo-3-propene was thermolyzed in the presence of nitric oxide (^{15}NO) the products consisted of nitrogen and isobutene. The rate of the noninhibited reaction was 50% faster than that in the presence of nitric oxide. Mass spectrometric inspection of the nitrogen produced indicated that much of the nitrogen, 10–18%, was derived from the nitric oxide. The activation parameters and rate constants at various temperatures for **8** are also collected in Table VII. Because of the large amounts of isobutene and $^{30}N_2$ observed in these runs a sample of nitroso-*tert*-butane was allowed to react with labeled nitric oxide and the

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The fraction of peak 28 (or 29) derived from the 0.4 mol % ^{14}NO is $0.004P_{30}/P_{28}$ and is not significant.

(26) R. C. West, "Handbook of Chemistry and Physics," 49th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1968, p B-4.

(27) While Forst and Rice [14a] observed some evidence for nitric oxide acting as an initiator at higher pressures, and at 250–300°, a control run with azomethane at 130° indicated that NO does not initiate thermolysis of azo compounds at the lower temperatures used here.

(28) A. Maschuke, B. S. Shapiro, and F. W. Lampe, *J. Amer. Chem. Soc.*, **85**, 1876 (1963). The nitroso compounds formed by reactions 18 and 19 may add radicals to *O*-alkylhydroxylamines, *e.g.*, R_2NOR.

(29) M. I. Christie, *Proc. Roy. Soc., Ser. A*, **249**, 248 (1958).

Table VIII. Reaction of $(CH_3)_3C^{14}NO$ (7.22 μmol) with ^{15}NO (29.2 μmol). Product Material Balance

Temp, °C	Time, hr	N_2, μmol	N_2O/N_2	C_4H_8[a]$/N_2$	^{15}NO[b]$/N_2$	Mass anal.	
						Rel ^{28}p	^{29}p = 100 ^{30}p
25.0	16	6.63	0.077	0.437	2.28	12.5	18.7
91.1	0.66	6.98	0.053	0.432	2.21	6.35	11.8
25.0	1.0[c]	4.52	0.067	0.705	2.72	2.72	2.9

[a] Isobutene. [b] Amount of NO consumed. [c] Stored at −194° after preparation.

Table IX. Rate Constants (Sec^{-1}) for the Thermolysis of **6**, **7**, and **8** at 122.3°

Azo-alkane	Calculated				Obsd	Rel rate[a]
	Eq 3		Eq 17			
	Lower limit	Upper limit	Lower limit	Upper limit		
6	1.0×10^{-10}	6.7×10^{-8}	1.8×10^{-6}	1.8×10^{-4}	4.90×10^{-6}	0.138
7	2.1×10^{-9}	2.9×10^{-7}	1.8×10^{-6}	1.8×10^{-4}	1.20×10^{-5}	0.339
8	1.4×10^{-7}	1.4×10^{-5}	1.8×10^{-6}	1.8×10^{-4}	1.74×10^{-4}	4.92
5					3.55×10^{-5}	1.00

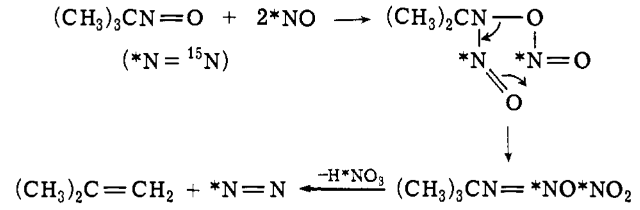
[a] Relative to **5**, see ref 4.

nitrogen produced was submitted for mass analysis. The results in Table VIII indicate that the peak of mass 29 is the largest. Levy and Copeland[3] reported that the thermolysis of 2,2′-azoisobutane in the presence of nitric oxide gave not only isobutene but also nitroso-*tert*-butane and proposed the following mechanism although they did not detect nitrous oxide (N_2O). The

$$(CH_3)_3C\cdot + \cdot NO \longrightarrow (CH_3)_2C{=}CH_2 + HNO \qquad (20)$$

$$2NO \longrightarrow N_2O + H_2O \qquad (21)$$

predominant formation of $^{14}N^{15}N$ is not compatible with this mechanism which should produce nitrous oxide. The following mechanism is consistent with the fate of the nitroso compound in the presence of labeled nitric oxide, and rationalizes the large amount of isobutene produced under these conditions. The formation of $^{14}N^{14}N$ and $^{15}N^{15}N$ in minor amounts is possibly due to the slow exchange reaction between the nitroso compound and the nitric oxide.[30]



Mechanism of Azoalkane Thermolysis. In solution there is good evidence for a concerted cleavage of both carbon–nitrogen bonds,[10] eq 1, in symmetrical azo compounds, and for a stepwise process, eq 2, for unsymmetrical azo compounds.[6,7,8b,10] The objective of this work is to examine azo compounds that will assist the choice between eq 1 and eq 2 for the gas-phase thermolysis of symmetrical and unsymmetrical azoalkanes.

What difference can we expect from eq 1 and eq 2? Ramsperger's criteria for the former was that the activation energy for the unsymmetrical azoalkane, R—N=N—R′, would be the mean of the activation energies of R—N=N—R and R′—N=N—R′. Using our knowledge of **1** and **5** we can readily estimate the rate of such a concerted process for **6**. The upper limit in the range displayed in Table IX for eq 1 was obtained for **6** by using the activation parameters of Rice and Sickman[31] and averaging them with the parameters for **5**.[4d] An allowance for steric factors was then made by increasing the calculated value tenfold to 5.90×10^{-8} sec^{-1}. The lower limit was calculated by using that set of data[14] which upon extrapolation to 120° gave a minimum rate constant for **1** and then multiplying it by 0.1 to allow for steric factors.[32] The same procedure was used in calculating the limits for **7**, the upper limit coming from the data of Geiseler and Hoffmann[33] under static conditions, and the lower limit, or minimum extrapolated rate for azo-1-propane, from the same authors' flow data. The range of rate constants for the applicability of eq 1 to **8** was calculated using the data of Levy and Copeland.[3] If eq 2 most clearly approximates the reaction mechanism, then a statistical factor of one-half need only be applied to the thermolysis rate of **5** to estimate that of **6**; and the same is true for **7** and **8**, applying a steric factor of ten gives the range quoted for eq 2 in Table IX.

It may be clearly seen that changing the alkyl group in the series from methyl, in **6**, to allyl in **5**, has little or no effect upon rate even though the corresponding bond dissociation energy for the analogous R–H bonds differs by 19 kcal mol^{-1}. A concerted process would be expected to increase the rate significantly upon the introduction of the second allyl group. The difference between **5** and **7** is only 2.96-fold, and the statistical factor reduces this to 1.48, a difference that is observed in diastereomeric azo compounds. It is reasonable to assume that the steric difference between *n*-propyl and allyl may be that large. Most significantly, if the diallyl compound is proceeding by only a factor of 1.48 times faster than **7** then it too must be proceeding by the stepwise mechanism, eq 2. Since the symmetrical azo compounds give rise to a good Polanyi plot,[4d] and **5** fits on that plot, then it is reasonable to assume that all of those compounds which have been thoroughly studied so as to remove any component of chain-

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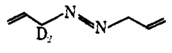
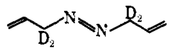
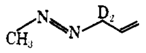
(30) B. G. Gowenlock, *Progr. React. Kinet.*, **3**, 17 (1965).

(31) O. K. Rice and D. V. Sickman, *J. Chem. Phys.*, **4**, 242 (1936); of the values in the literature for **1** these parameters give the maximum rate constant upon extrapolation to 122.3°.

(32) Such a process sets generous limits upon the range of rates in which we expect eq 1 to hold. The factor 10, although somewhat arbitrary, was decided upon after considering the data in Tables I and II.

(33) G. Gieseler and J. Hoffmann, *Z. Phys. Chem.*, **57**, 318 (1968).

Table X. Secondary Deuterium Kinetic Isotope Effects on Allylic Azo Compounds

Azo compound	Temp, °C	$(k_H/k_D)_{obsd}$	$\Delta\Delta G^{\ddagger}$ per deuterium, cal mol^{-1} Eq 3	Eq 17
	161.65	1.14 ± 0.02^a	56 ± 8	121 ± 18
	161.65	1.26 ± 0.02^a	50 ± 4	99 ± 9
	126.00	1.28 ± 0.05^b		98 ± 15

^{a} See ref 4. ^{b} After correction for nitrogen produced from ^{15}NO; see text.

induced decomposition, **1**, **4**, **5** and azoethane[34] also undergo thermolysis by the same mechanism.

Using the group additivity values of Benson and O'Neal[12] the following thermochemistry is obtained, where $\Delta H° = 37 \pm 2$ kcal mol^{-1}

$$\underset{+53}{CH_3CH_2CH_2N{=}NCH_2CH{=}CH_2} \longrightarrow \underset{+52}{C_3H_7N_2\cdot} + \underset{+38^{35}}{\text{allyl}\cdot}$$

The good agreement between the calculated value of $\Delta H°$ for the initial cleavage step and $\Delta H^{\ddagger}{}_7$ of 36.3 $\pm$ 0.5 kcal mol^{-1} implies that the transition state is best described as being that wherein the allylic carbon–nitrogen bond is completely ruptured. Because azoalkanes can exist in the cis (*Z*) or trans (*E*) form[36,37] and because the *Z* isomers have been observed to undergo thermolysis more rapidly than the *E* isomer[37] the possibility exists that the similarity of the activation free energies for **6**, **7**, and **8** could arise from a rate-determining geometrical isomerization, $E \rightarrow Z$ (since in each case the allylic group is involved), followed by a rapid thermolysis of the *Z* isomer.[37] That the geometrical isomerization is not rate determining is demonstrated by the existence of a secondary deuterium kinetic isotope effect (see next section) for **14**. It also seems improbable that the reactivity order of such an isomerization would be **8** > **7** > **6**, the opposite to the order expected on steric grounds.[38]

Examining the azoalkanes **6** and **7** in terms of a Polanyi plot that allows for some concertedness, *e.g.*, as per expression 3, and assuming that $\alpha + \alpha' = 1.0$ and $C = 48.4$, the slope and intercept observed for the Polanyi plot correlating symmetrical azoalkanes, then the nonsymmetrical compounds are fit only if $\alpha = 1.0$ and $\alpha' = 0$. Because of the experimental error in obtaining activation energies and the precision to which we know bond dissociation energies[4c] we can allow values such as $\alpha = 0.9$ and $\alpha' = 0.1$ but a greater degree of concertedness such as $\alpha = 0.8$ and $\alpha' = 0.2$ requires activation energies outside the experimental error.[39] If there is any concertedness then it must be very small by this criteria.

A further test of the appropriateness of eq 2 is readily available by examining the magnitude of the secondary deuterium isotope effects of methylazo-3-propene-*3,3-d*$_2$ (**14**). The nitric oxide inhibited thermolysis of **6** and **14** was examined in parallel runs at 126.0° using ^{15}NO. The amount of nitrogen produced was measured volumetrically and then analyzed by mass spectrometry. The fraction of nitrogen derived from **6** and **14** was then calculated and plotted in the usual manner. Table X compares the results from **14** with those of previously reported results for the thermolysis of deuterated azo-3,3'-propenes.[4] The values obtained by assuming that only one nitrogen–carbon bond of **5** is being ruptured in the rate-determining step are more consistent with that derived from **14** and those generally found for thermolysis processes ($\Delta\Delta G^{\ddagger} =$ 80–120 cal mol^{-1}).[10,40]

$$\underset{\textbf{14}}{CH_3N{=}NCD_2CH{=}CH_2}$$

The activation energy for the *tert*-butylazo-3-propene seems to be lower than that which one might expect, from a strictly statistical treatment of the rate processes, for a stepwise mechanism. This may be due to steric factors which are relieved in the transition state. It is difficult to see exactly how these steric factors would operate unless the resulting radical RN=N· has a larger C–N–N bond angle in the transition state than in the ground state.[37b] The log *A* term for **8** seems to similarly be smaller than expected, and there may be some compensation between these. It is certainly true that the study of **8** was complicated by the amount of nitrogen produced from the nitric oxide and by the low vapor pressure of **8**. There is no evidence in this study to indicate that the nitrogen-containing radical is an intermediate; if it is then it is probably very short lived, for as Benson and O'Neal[12] have pointed out the second step should be very exothermic; *e.g.*, for **6**, CH_3–$N_2\cdot$ (+62) $\rightarrow$ $CH_3\cdot$ (+34) + N_2, $\Delta H = -28$ kcal mol^{-1}.

It is apparent that in the gas phase few, if any, of the azoalkanes undergo a concerted thermolysis to produce three fragments. It is similarly apparent that in the case of some cyclic systems, *e.g.*, **15**, concertedness is indeed operative. The double bond in **15** makes both carbon–nitrogen bonds allylic and the decrease in activation energy,[41] if the reaction is stepwise, may be compared with that on going from azo-1,1'-pro-

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[34] H. S. Sandhu, *J. Phys. Chem.*, 72, 1857 (1968); W. D. Clark, Ph.D. Dissertation, University of Oregon, Eugene, Ore., 1959.

[35] W. Tsang, *Int. J. Chem. Kinet.*, 1, 245 (1969).

[36] R. F. Hutton and C. Steel, *J. Amer. Chem. Soc.*, **86**, 745 (1964).

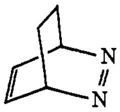
[37] (a) T. Mill and R. S. Stringham, *Tetrahedron Lett.*, 1853 (1969); (b) N. J. Porter, L. J. Marnett, C. H. Lockmüller, G. Closs, and M. Shobataki, *J. Amer. Chem. Soc.*, **94**, 3664 (1972).

[38] If we have two completely dissociated fragments as the transition state then the only stereochemical conclusion that we can draw from the kinetic evidence herein is that the activation energy corresponds to the difference in energy between the ground state, the *E* isomer, and the transition state having no *Z* or *E* stereochemistry but only that of the bent R'—N=N· radical[37b] and the allyl radical.

[39] If we use the bond dissociation energies for CH_3–H of 104 and 85 kcal mol^{-1} for $CH_2{=}CHCH_2$–H then expression 1 becomes $E_a{}^6 =$ 0.8(85) + 0.2(104) − 48.4 which gives 40.4 kcal mol^{-1} for **6** and 38.4 for **7**.

[40] E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 109 (1963): A. A. Zavitas and S. Seltzer, *J. Amer. Chem. Soc.*, **86**, 1265 (1964); S. E. Scheppele, *Chem. Rev.*, in press.

[41] N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *J. Amer. Chem. Soc.*, 91, 5668 (1969), have estimated $\Delta H^{\ddagger}{}_{15}$ to be less than 16 kcal mol^{-1}.



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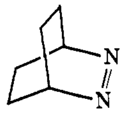

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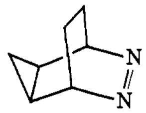

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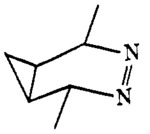

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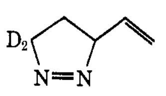

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pane[38] to azo-3,3′-propene[4] (**5**), a decrease of 10 kcal mol^{-1}. The observed decrease is nearly three times that amount, $\Delta H^{\ddagger}_{16} - \Delta H^{\ddagger}_{15} = 29$ kcal mol^{-1}. While in **15** the ideal conformation for the concerted bond rupture is built directly into the system a concerted process for **5** would require precisely the correct rotational conformation at both carbon–carbon single bonds in the allyl groups, and possibly around the azo nitrogens. The low activation energies observed for **17**[42] and the stereospecificities and rapid reaction rates observed for **18**[43] suggest that they are also concerted. There is only a 6 kcal mole^{-1} decrease in activation energy on going from azoethane to 1-pyrazoline,[44] and in view of the steric factors imparted by methyl substitution, the decision that both carbon–nitrogen bonds are breaking in the rate-determining step is not as secure as it first seemed. There is some support for the formation of two fragments, *i.e.*, concerted cleavage of both carbon–nitrogen bonds in the cyclic system, from the secondary deuterium kinetic isotope effects on substitution in the α position[45] of 1-pyrazoline and from the secondary deuterium kinetic isotope effects on the thermolysis[46] of **19**. We are, however, investigating other methods for the assessment of concertedness in the thermolysis of 1-pyrazoline.

Experimental Section

All boiling points and melting points are uncorrected. The nuclear magnetic resonance spectra were obtained using Varian A-60 and HR-100 spectrometers. Exact masses were measured on an AEI MS-9 mass spectrometer. Product analyses were carried out on an AEI MS-12 mass spectrometer, of which the ion source was coupled by means of a Watson-Biemann helium separator to an Aerograph Model 1200 Hi-Fi gas chromatograph. Isotope ratio measurements of nitrogen were carried out on a CEC 21-614 mass spectrometer. Sample purifications and product analyses were carried out on a gas chromatograph coupled directly into the vacuum line.

The vacuum line used herein was similar to that described by Forst and Rice.[14] The Bourdon gage and volumes were all calibrated and greaseless valves were used throughout.[47]

The reactions were carried out in a well insulated covered oil bath. The temperature was controlled by a Melabs proportional temperature controller, and was measured using a Hewlett-Packard 2801A (NBS) quartz thermometer. The oil bath temperature was maintained to within ±0.02°.

Kinetics. The rate of the reaction was determined by measuring the amount of nitrogen produced from a known quantity of azoalkane. A sample run is given in Table XI. The reaction was tested for any surface effects by measuring the rate in the presence of glass wool, and, as has been observed for other azoalkanes, no surface catalysis was noticed.[1,3,14] Because of the restraints upon the amount of nitric oxide the reactions were only run to 5% conversion.

Table XI. Sample Kinetic Data for the Thermolysis of **6**, at 125.90° (Initial Total Pressure, 57 Torr, NO; **6** of 0.197)

Time, sec	Amount of **6**, mol	Nitrogen prod, mol	$10^2 \cdot R^a$	$-\log (1 - R)$	$10^6 k$, sec^{-1}
1200	40.2	0.34	0.85	0.00371	7.14
2400	40.4	0.73	1.81	0.00793	7.62
3600	39.6	1.17	2.96	0.0130	8.37
4800	39.6	1.46	3.69	0.0163	7.83
6000	39.5	1.85	4.68	0.0208	7.99
7200	39.6	2.52	6.37	0.0286	7.83
				Av	7.80

[a] R = amount of N_2 produced/initial amount of **6**.

Method of Product Analysis. After the reaction the breakseals were connected to the vacuum manifold and ruptured by a piece of magnet covered with glass. The nocondensable gases (nitrogen and methane) were pumped off by means of a Toepler pump and measured in a gas buret before their analysis by gc. The condensable gases were then analyzed in a similar manner. In the case of the products arising from **8** the C_6–C_8 fractions were trapped in a pentane–Dry Ice slurry and then analyzed.

When nitric oxide or xenon was present as a foreign gas, a solid nitrogen trap (−210°) was added to the sequence to remove all of the NO. For mass spectrometric analysis of the nitrogen, the nitrogen collected in the gas buret was transferred to a breakseal by means of a Toepler pump and then attached to the mass spectrometer's inlet system.

Gas Chromatography. The noncondensable fraction (methane and nitrogen) was analyzed on a 5 ft × 1/4 in. glass column filled with 40–60 mesh high activity charcoal (Burrell). The column was calibrated for nitrogen and methane by injecting a known amount of each gas onto the column and measuring the corresponding peak area. Peak areas were measured by multiplying the peak height by the width at half-height. Seven calibration points were obtained for nitrogen, spaced over the range 16–67 μmol; nine calibration points were obtained for methane, over the range 1.4–10 μmol. The calibration was linear over the entire range and calibration factors determined by the method of least squares show a standard deviation of 2.6% for nitrogen and 4.9% for methane. The ratio of calibration factors (= ratio of sensitivity) for nitrogen and methane was 1.12, in good agreement with the figure 1.14 determined by Forst and Rice.[14]

Condensable gases obtained in the thermolysis of methylazo-3-propene were analyzed on a 10 ft × 1/4 in. glass column filled with 20% dimethylsulfolane on 30–60 mesh Chromosorb P (Johns-Manville). The column was calibrated for 1-butene, 1,5-hexadiene, and azomethane at room temperature. The ratios of sensitivities of 1-butene to 1,5-hexadiene, and 1-butene to azomethane, were 0.83 and 1.11. This column was capable of separating ethane, carbon dioxide, propene, cyclopropane, 1-butene, allene, *n*-pentane, azomethane, 1,5-hexadiene, and methylazo-3-propene, but not ethene- or carbon dioxide–nitrous oxide mixtures at room temperature. The ethane–ethene mixture was separated using an activated aluminum column at 0°. A 6 ft × 1/4 in. glass column filled with 30–60 mesh silica gel (Hewlett Packard) was capable of separating small amounts of ethane from xenon.

The C_4 components (isobutane and isobutene) obtained in the thermolysis of *tert*-butylazo-3-propene were analyzed on a 10 ft × 1/4 in. glass column filled with 20% dimethylsulfolane (F & M Scientific) on 30–60 Chromosorb P. The C_6–C_8 components (1,5-hexadiene, 4,4-dimethyl-1-pentene, and 2,2,3,3-tetramethylbutane) were analyzed on a 3 ft × 1/4 in. glass column filled with 20% dimethylsulfolane on 30–60 mesh Chromosorb P. This column was capable of separating 1,5-hexadiene, 2,2′-azoisobutane, and *tert*-butylazo-3-propene.

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Preparation of Diethyl *N*-Allyl-*N′*-methylbicarbamate. Sodium hydride (9.9 g of a 53.8% slurry, 0.216 mol) was added to a mixture of diethyl *N*-allylbicarbamate[4d] (44.5 g, 0.206 mol) in 300 ml of dimethoxyethane. The solution was maintained at room temperature under a blanket of nitrogen and stirring was continued for 3 hr after the addition of methyl iodide (60 g, 0.422 mol) had been completed. After stirring overnight the mixture was treated with ice water and the product was extracted with benzene. The benzene solution was dried over potassium carbonate and the solvent was removed on a rotary evaporator. The residue separated into two layers and the upper layer (the mineral oil from the sodium hydride) was discarded. The lower layer was fractionally distilled through a 30-cm Vigreux column and each fraction was analyzed by gc (10 ft, 7% Carbowax columns at 150°). After a small forerun there was obtained a 35-g (74%) sample, bp 72–73° (0.05 Torr), free from impurities. The nmr spectrum displayed signals at δ 1.25 (t, 6 H, ester methyls), 3.08 (s, 3 H, NCH_3), ~4.2 (overlapping d and q, 6 H, allylic and ester methylenes), ~5.2 (m, 2 H, vinylidene), and ~5.9 (m, 1 H, methine).

Anal. Calcd for $C_{10}H_{18}O_4N_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.16; H, 7.96; N, 12.29.

Preparation of Methylazo-3-propene (6). A slow stream of nitrogen was bubbled through 100 ml of warm ethylene glycol for 20 min in a mechanically stirred three-necked flask. The gas inlet tube was replaced with a condenser and a thermometer, and potassium hydroxide (9.52 g, 0.168 mol) was added in four portions. The ethylene glycol solution was heated to 125° and **9** (8.5 g, 0.37 mol) was added as rapidly as possible to the stirred solution. After the addition, the temperature of the reaction was maintained at 125–130° for 1 hr. After being cooled, the mixture was cautiously added to 50 g each of ice and water and 30 ml of 12 *N* hydrochloric acid. The ethylene glycol and water were distilled off at 1–2 Torr. The distillation residue was dissolved in water and extracted with ether. The ether extract contained a small amount of brown oil. The aqueous solution was basified with potassium hydroxide (5.0 g) and then extracted overnight with ether using a continuous extractor. The ether was distilled off through a Vigreux column. An aliquot of the residue was shaken with diluted hydrochloric acid and then the excess hydrochloric acid and water were distilled off at 90° (2.0 Torr). The nmr spectrum of the hydrazine hydrochloride displayed signals at δ 2.81 (s, 3 H, NCH_3), 3.67 (d, 2 H, allyl), 4.84 (s, 4 H, N^+H_2), and 5.6 (m, 3 H, vinyl).

A solution of the crude hydrazine in ether (50 ml) was treated with a well-stirred slurry of red mercuric oxide (50 g, 0.23 mol) and anhydrous sodium sulfate (10 g). After 5 hr the solution was filtered and the azo compound was separated by preparative gc. The yield was 0.9 g (20% yield based on **9**).

The nmr spectrum displayed signals at δ 3.78 (s, 3 H, *N*-methyl), 4.46 (d, 2 H, allylic methylene), ~5.3 (m, 2 H, vinylidene), and ~6.1 (m, 1 H, methine). The uv spectrum has a λ_{max} at 345 nm (ϵ 20 in the gas phase). The mass spectrum gave a parent peak at mass 84.0687 (calcd for $C_4H_8N_2$, 84.0688).

Diethyl *N*-(Allyl-1,1-d_2)-*N′*-methylbicarbamate. Sodium hydride (0.05 g of a 57.2% slurry, 25 mmol) was added to a well-stirred mixture of diethyl *N*-methylbicarbamate (4.75 g, 25 mmol) in 40 ml of dimethoxyethane. The solution was stirred at room temperature under a nitrogen atmosphere for 3 hr. Allyl-*1,1*-d_2 benzenesulfonate[4] (5 g, 25 mmol) in 10 ml of dimethoxyethane was then added and the solution stirred for an additional 4 hr. After standing overnight the reaction mixture was treated with ice–water and the product was extracted with benzene. The benzene solution was dried over potassium carbonate and the solvent was removed by distillation. The residue separated into two layers and the upper layer (the mineral oil from sodium hydride) was discarded. The lower layer was fractionally distilled through a 30-cm Vigreux column and each fraction was analyzed by gc.

After a small forerun a 3.0-g (52%) sample, bp 80° (1 Torr), free from impurities, was obtained. The late fractions (1.0 g) were contaminated with 30% of the unreacted starting material. The nmr spectrum displayed signals at δ 1.27 (t, 6 H, ester methyls), 3.11 (s, 3 H, NCH_3), 4.2 (q, 4 H, ester methylene), ~5.2 (m, 2 H, vinylidene), ~6.1 (m. 1 H, methine), and no allylic hydrogens at 4.46 (less than 2%). The mass spectral analysis showed a molecular ion which has a mass of 86.0816 (calcd for $C_4H_6N_2D_2$, 86.0813).

Preparation of Diethyl *N*-Allyl-*N′*-(1-propyl)bicarbamate. Sodium hydride (2.53 g of a 57.2% slurry, 60.2 mmol) was added to a well-stirred solution of diethyl *N*-allylbicarbamate (13.0 g, 60.2 mmol) in 100 ml of dimethoxyethane. The solution was maintained at room temperature under a protective atmosphere of nitrogen and stirring was continued for an additional 3 hr. *n*-Propyl bromide (10 g, 0.0813 mol) and potassium iodide (1 g, 6 mmol) were then added and the solution stirred for 10 hr. An aliquot was taken out from the reaction mixture and after being treated with water, analyzed by gc (10-ft SF-96, 150°); 40% of the starting material was found unreacted. *n*-Propyl iodide (5.1 g, 30 mmol) was added to the reaction mixture. The reaction was found to be complete after the solution was stirred for an additional 20 hr. The mixture was treated with ice–water and the product was extracted with ether. The ether solution was dried over potassium carbonate, the solvent was removed on a rotary evaporator, and the product was purified by distillation through a 30-cm Vigreux column, which gave 7.0 g (45% yield), bp 94–95° (1.0 Torr). The nmr spectrum displayed signals at δ ~1.25 (overlapping t and sextet, 1 H, $\mathit{CH_3CH_2}\mathrm{CH_2N}$ and $\mathit{CH_3}\mathrm{CH_2O}$), 3.43 (distorted t, 2 H, $\mathrm{CH_3CH_2}\mathit{CH_2}\mathrm{N}$), ~4.19 (overlapping d and q, 6 H, allyl and $\mathrm{CH_3}\mathit{CH_2}\mathrm{O}$), ~5.15 (m, 2 H, vinylidene), ~5.9 (m, 1 H, methine). The mass spectrum gave a parent peak at mass 258.1576 (calcd for $C_{12}H_{22}N_2O_4$, 258.1580).

Preparation of 1-Propylazo-3′-propene (7). A slow stream of nitrogen was bubbled through 70 ml of ethylene glycol for 20 min in a mechanically stirred flask with mild heating. Potassium hydroxide (6.7 g, 0.118 mol) was then added and the solution was heated to 125° before diethyl *N*-allyl-*N′*-(1-propyl)bicarbamate (6.7 g, 0.026 mol) was added as rapidly as possible to the stirred solution. After addition the solution was stirred at 125–130° for 1 hr under a nitrogen atmosphere. Upon being cooled, the mixture was cautiously added to 35 g each of ice and water and 21 ml of 12 *N* hydrochloric acid. When acidification was complete, the mixture was warmed to about 40° and the water and ethylene glycol were distilled off at 1–2 Torr. The solid residue obtained was dissolved in 70 ml of water and then extracted with ether. The evaporation of the ether gave 1 g of the starting material. The aqueous solution was basified by solid potassium hydroxide. 1-Allyl-2-(1-propyl)hydrazine was extracted with ether using a continuous extractor. The ether solution was dried over anhydrous sodium sulfate and used immediately for oxidation to **7**.

The ether solution of 1-allyl-2-(1-propyl)hydrazine was stirred with a slurry of red mercuric oxide (10 g, 46 mmol) and anhydrous sodium sulfate (20 g) for 4 hr. The ether was condensed to 3 ml through a 30-cm Vigreux column. A gas chromatographic analysis showed that the condensed solution contained *ca.* 20% of 1-propylazo-3′-propene (**7**) which was separated by gc using a 20%, 6-ft, β,β'-oxydipropionitrile column on Chromosorb P.

The nmr spectrum displayed signals at δ 0.97 (t, 3 H, $\mathit{CH_3}\mathrm{CH_2CH_2N}$), 1.82 (sextet, 2 H, $\mathrm{CH_3CH_2}\mathit{CH_2}\mathrm{N}$), 3.76 (t, 2 H, $\mathrm{CH_3CH_2}\mathit{CH_2}\mathrm{N}$), 4.40 (d, 2 H, allyl methylene), ~6.2 (m, 1 H, methine). The uv spectrum has a λ_{max} at 355 nm (ϵ ~20 in the gas phase). The mass spectrum gave a parent peak at 112.1008 (calcd for $C_6H_{12}N_2$, 112.1001).

Preparation of Dimethyl *N*-*tert*-Butylbicarbamate. *tert*-Butylhydrazine hydrochloride[14] (8.8 g, 70.7 mmol) was dissolved in 50 ml of water. Solid sodium hydroxide (6 g, 0.15 mol) was then added to the solution. *tert*-Butylhydrazine was extracted by ether using a continuous extractor for 10 hr.

The ether solution (50 ml) of *tert*-butylhydrazine was placed in a 300-ml Morton flask. When the stirred mixture had cooled to 5°, methyl chloroformate (13.2 g, 0.14 mol) was added without allowing the temperature to rise above 5°. When almost half of the chloroformate had been added, a cold solution of sodium hydroxide (5.6 g, 0.14 mol) in 10 ml of water was added gradually along with the rest of the chloroformate at such a rate that the final portions of the two solutions were added simultaneously. After standing for 15 min the ether layer was separated and the aqueous solution was extracted with ether. The combined ether layers were rapidly dried by shaking for a short time with about 1 g of sodium carbonate in two portions. On evaporation of the ether the crude solid product (8 g) was obtained. After a small amount (*ca.* 0.3 g) of benzene-insoluble impurity was removed the product was crystallized from benzene–hexane, mp 82–83°. The yield was 6.5 g (45%).

The nmr spectrum displayed signals at δ 1.41 (s, 9 H, *tert*-butyl), 3.69 (s, 3 H, ester CH_3), 3.76 (s, 3 H, ester CH_3), and 7.40 (br s, exchangeable with D_2O–NaOD, 1 H, NH). The mass spectrum gave a parent peak at mass 204.1106 (calcd for $C_8H_{16}N_2O_4$, 204.1110).

Preparation of Dimethyl *N*-Allyl-*N′*-*tert*-butylbicarbamate. Sodium hydride (1.23 g of a5 7.2% slurry, 30 mmol) was added to a mixture of dimethyl *N*-*tert*-butylbicarbamate (6.0 g, 29.4 mmol) and 50 ml of dry dimethoxyethane. The solution was maintained at room temperature under a blanket of nitrogen and stirring was continued for 3 hr. Allyl bromide (4 g, 33 mmol) was then added and the solution stirred for an additional 4 hr. After standing overnight the reaction mixture was treated with ice and water and the product was extracted with benzene. The benzene solution was dired over anhydrous sodium sulfate and the solvent was removed on a rotary evaporator. The crude product was distilled through a Vigreux column and the fraction which boiled at 90° (1.8 Torr) was collected. The yield was 6.0 g (84%). The nmr spectrum displayed signals at δ 1.39 (s, 9 H, *tert*-butyl), 3.68, 3.74, and 3.78 (s, 6 H, ester methyls), 4.04 (d, 2 H, allylic methylene), ~5.2 (m, 2 H, vinylidene), and ~6.0 (m, 1 H, methine). The two singlets at δ 3.78 and 3.74 were found to coalesce at 40–35°. The mass spectrum gave a parent peak at mass 244.1418 (calcd for $C_{11}H_{20}N_2O_4$, 244.1423).

Preparation of *tert*-Butylazo-3-propene (8). A slow stream of nitrogen was bubbled through 60 ml of ethylene glycol for 20 min in a mechanically stirred flask with mild heating. Potassium hydroxide (6.07 g, 107 mmol) and dimethyl *N*-allyl-*N′*-*tert*-butylbicarbamate (1.7 g, 23.6 mmol) were added. The mechanical stirrer was replaced with a Liebig condenser. The hydrazine, along with the methanol formed, was distilled under a stream of nitrogen at the bath temperature of 150–160°. Concentrated hydrochloric acid was added to the distillate to give, upon further evaporation, 1.7 g of 1-allyl-2-*tert*-butylhydrazine hydrochloride, mp 165–175°. The nmr spectrum in D_2O displayed signals at δ 1.37 (s, 9 H, *tert*-butyl), 3.64 (d, 2 H, allylic methylene), 4.74 (s, 4 H, NH), ~5.5 (m, 2 H, vinylidene), and ~5.8 (m, 1 H, methine). The yield was 36%.

Potassium hydroxide (3 g, 60 mmol) was added to a solution of the hydrochloride of the hydrazine (1.7 g, 8.45 mmol) in 20 ml of water. The hydrazine was extracted with ether and the ether solution dried over anhydrous sodium carbonate. The dried solution of the hydrazine (8.45 mmol) in ether (50 ml) was stirred at room temperature with a slurry of red mercuric oxide (10 g, 46 mmol) and anhydrous sodium sulfate (20 g). After 6 hr the solution was filtered and concentrated to 2 ml by distillation through a Vigreux column, and the azo compound **8** was separated by gc using a 2-ft column of 20% dimethylsulfolane on Chromosorb P at room temperature. The yield was 0.8 g (75%). The nmr spectrum displayed signals at δ 1.19 (s, 9 H, *tert*-butyl), 4.34 (d, 2 H, allylic methylene), ~5.2 (m, 2 H, vinylidene), and ~6.2 (m, 1 H, methine). The uv spectrum has a λ_{max} at 355 nm (ε ~25 as a gas). The mass spectrum gave a parent peak at mass 126.1159 (calcd for $C_7H_{14}N_2$, 126.1157).

Control Experiments. (a) Mass Spectrometric Analysis of Nitrogen and Isotope Nitric Oxide (^{15}NO). The mass spectrometric analyses of pure nitrogen, and of nitrogen produced from **6** and **8**, were found consistent with the natural abundance of nitrogen ($^{14}N^{15}N/^{14}N^{14}N = 7.4 \times 10^{-3}$ and $^{15}N^{15}N/^{14}N^{14}N$ = nil).[26] Scrambling between ^{15}NO and N_2 under the reaction conditions could not be detected (<0.1%).

(b) Reaction of 1-Butene with Nitric Oxide. The reaction of 1-butene with NO was carried out in order to test the inertness of the olefinic bond under the thermolysis conditions. The olefinic bond was found to be stable to NO at 130° which is the highest temperature used for the study of the inhibited thermolysis of azo compounds. A sample left at 145° for 10 hr did show a loss in butene and 4% of the nitric oxide was converted to nitrogen.

(c) Nmr Analysis of the Recovered Methylazo-3-propene-*3,3*-d_2 (14). Mixtures of **14** and ^{15}NO (29.1–31.4 μmol of **14**, ^{15}NO/**14** = 0.161) were thermolyzed at 126.00° for 30–130 min. The unreacted **14** was collected and analyzed by 100-MHz nmr. The signal at δ 4.46 for allylic protons was completely absent indicating that no scrambling was observed under these conditions.

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Rearrangement of *N*,*N*-Dichlorotri-*n*-butylcarbinamine by Aluminum Chloride[1]

Timothy A. Kling,[2] Ronald E. White,[3] and Peter Kovacic*

Contribution from the Department of Chemistry,
University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201.
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Abstract: Treatment of *N*,*N*-dichlorotri-*n*-butylcarbinamine with aluminum chloride in methylene chloride, followed by acid hydrolysis, produced di-*n*-butyl ketone and *n*-butylamine in yields of 95 and 92%, respectively. Careful control of variables during rearrangement and work-up was necessary for best results. Optimum yields were realized at −30° followed by steam distillation during hydrolysis. The mechanistic interpretation involves abstraction of chloride ion by aluminum chloride and migration of an alkyl group from carbon to electron-deficient nitrogen. Hydrolysis of the rearranged product presumably generates a carbinolamine which decomposes to the ketone and amine. Supporting evidence is discussed, including literature analogy. This comprises the first example of a 1,2 shift to positive nitrogen derived from a simple, open-chain *N*-haloalkylamine.

Many articles and reviews have dealt with rearrangements involving migration of an alkyl group from carbon to an electron-deficient atom. Carbon to carbon migrations which are well established include the Wagner-Meerwein and pinacolic types.[4] Alkyl shift from carbon to oxygen is also known,[5] as exemplified by the Baeyer-Villiger oxidation. Carbon to nitrogen rearrangement[6] has been observed with various substrates, such as azides, hydroxylamines, and haloamines. Rearrangements involving *N*-haloamines[7] include the Hofmann-Löffler reaction,[8] conversion of *N*,*N*-dichloro-*sec*-alkylamines to α-amino ketones,[9] and intermediacy of nitrenium ions.

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